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A PERSON PORTABLE ANALYTICAL SYSTEM FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS

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A PERSON PORTABLE ANALYTICAL SYSTEM

FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS

by

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Abstract

A field usable, person portable analytical system (Level 2) for the determination of polychlorinated biphenyls (PCBs) in oil, water and soil, and from solid surfaces (e.g. concrete, asphalt, wood, etc.) has been developed. The test used in this system is based on the quantitative conversion of the chlorine atoms on chlorinated organic compounds to chloride ions. These ions are then extracted into an aqueous solution and measured by titrimetric means. The lowest limit of detection for Aroclor 1260 in oils using this titrimetric test has been determined to be 15 ppm and 35 ppm in soils. The highest detection limit determined has been greater than 35000 ppm. This method has an analysis time of less than 20 minutes and requires no sample preparation. It is non-specific in identifying Aroclor types, and chlorinated organic compounds, other than PCBs, can interfere with the chemical reactions.

RÉSUMÉ

On a mis au point un dispositif portatif (niveau 2), utilisable sur le terrain, pour l'analyse des biphényles polychlorés (BPC) présents dans les hydrocarbures, l'eau et le sol ainsi que sur les surfaces solides (p. ex., le béton, l'asphalte, le bois, etc.). Son principe de fonctionnement est de transformer les atomes de chlore d'un composé organique chloré en ions chlorure, de faire passer ceux-ci en solution aqueuse puis de les doser par titrimétrie. La limite inférieure de détection de l'Aroclor 1260 a été déterminée à 15 millionièmes (10^{-6}) dans les huiles et à 35×10^{-6} dans les sols. La limite supérieure a dépassé $35\,000 \times 10^{-6}$. Une analyse dure moins de 20 mn et n'exige aucune préparation de l'échantillon. Pour les Aroclor, la méthode n'est pas spécifique, et les autres composés organiques chlorés peuvent gêner l'analyse.

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INTRODUCTION

Although polychlorinated biphenyls (PCBs) have never been manufactured in Canada, approximately 40,000 tonnes were imported prior to the ban on importation. Of this amount approximately 24000 tonnes can be accounted for today. 61% are found in electrical transformers, 12% in electrical capacitors and 27% in storage waiting for disposal. The remaining 16000 tonnes has been dispersed into the environment (Dillon,1985).

PCBs have been frequently spilled. For the period of January, 1974 to December, 1983, PCB spill incidents numbered 333 and amounted to approximately 89 tonnes. This number represents the highest number of spill incidents recorded for this period of time (NATES, 1985).

Currently, the analysis procedure approved by both ASTM and EPA, for determining PCBs in dielectric fluids and soils is the extraction of the PCBs from the sample with an organic solvent followed by the subsequent analysis with packed column gas chromatography (GC) and electron capture (EC) detection. Sending an oil or soil sample to a commercial laboratory for such an analysis by GC-EC to see if regulations are met, could take several days to obtain results, depending on the laboratory's work load. Control of a spill site for this length of time could be a problem. Thus, what is needed is a field usable system which meets the following requirements:

- rapid detection of PCBs in water, soil and on surface materials (e.g. asphalt, cement and concrete),

- identification of PCBs concentrations in water and soil to determine the extent of environmental contamination from spills and to determine if they are within the levels specified by the regulations,

- monitoring capability within the levels specified by the regulations for clean-up purposes.

If such information is immediately available, environmental damage and human exposure to hazardous materials can be minimized. In addition, more cost-effective clean-up programs can be implemented if the amount and extent of contamination is known.

Two levels of analytical capability for the Environmental Emergencies Technology Division (EETD) priority list chemicals are being developed by EETD for the Canadian climate based on portability, accuracy and complexity. One of these is Level 2 which is a person-portable system. It is operable by non-technical personnel, and can employ electronic detection systems.

These systems minimize operator subjectivity, allowing more accurate quantitation. Although many Level 2 systems are non-specific with respect to substances detected, this does not represent a serious drawback since, in many spill situations, only one hazardous substance is involved, and concentration levels of this substance are likely to far exceed levels of potential interferences in the ambient background. These systems are not appropriate for verification and are to be used only to estimate concentrations. Important criteria to be met by Level 2 systems include:

a) rapidity in obtaining results
b) accuracy
c) ability to provide detection limits below maximum allowable limits for a wide range of hazardous substances of interest
d) simplicity of use and maintenance
e) moderate cost to allow for wide distribution across Canada.

One of the units selected for the Level 2 program is the HACH kit. The HACH portable laboratory kit contains a variety of pre-packaged analytical tests for water quality determination which can be reliably performed by non-technical personnel. The HACH tests are based on standard colourimetric reactions which are measured by a portable spectrophotometer or on titrimetric reactions. Direct concentration read-out ability of the kit, along with its portability, makes it attractive for spill response applications. While most of the commercially available tests are for inorganics in water, further modifications and development of the system allow for the analyses of many pollutants in water and soil Work by EETD in 1983-1987 has involved an evaluation of the HACH kit and a literature review of available analytical (wet test) techniques for the EETD priority chemicals (excluding PCBs) not covered by existing HACH kit tests. Numerous wet tests were selected from this review, and have been and are being evaluated.

The objective of this study was to modify and develop the existing HACH kit for use by the EETD Level 2 Analytical System for analysis of PCBs in oil, soil and water.

1. The initial step of this study was to review the literature on PCB analysis.

2. The next step was to select what methods could be tested in this study for analysis of PCBs in oil, water, and various types of soil,

3. The chosen analytical methods were assessed for their
   -accuracy
   -interferences
   -sensitivity
   -adaptability for field use

4. Following these evaluations a method, which may have been modified, was selected which could be included in a modified HACH kit.

5. The final step was to obtain calibration data for PCBs using these chosen methods and to convert them to a usable form for the spill responder.

Each of these steps will be described in detail and be discussed in the following sections.

ANALYTICAL METHODS FOR POLYCHLORINATED BIPHENYLS

To fully understand the analytical methods for PCB determination, it is necessary to know

- what are PCBs,
- what are the chemical formulations of PCB mixtures which may be found,
- what are the physical chemical properties of these mixtures, as well as those of the pure compounds,
- etc.

A brief summary of this information is given in this section.

Polychlorinated biphenyls (PCBs) are a class of 209 chemical compounds in which one to ten chlorine atoms are attached to each biphenyl group. The general structure is shown in Figure 1.

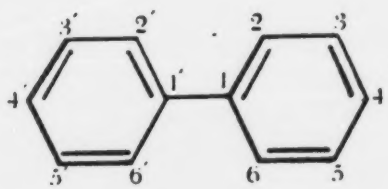


Figure1. Biphenyl Ring Numbering System

Selected physical-chemical properties of PCBs at 25 C are given in Table 1. Due to their chemical and physical stability and their electrical insulating properties, PCBs were commercially produced as complex mixtures and used for a variety of purposes (e.g. in transformers, capacitors, printing inks, paints, dedusting agents, pesticides) (Durfee, 1976). Technical PCB products were identified by the percentage of chlorine by weight in the mixture. The average composition of several Aroclors are shown in Table 2. Physical chemical properties of these mixtures are listed in Table 3. Other major technical PCB mixtures are listed in Table 4.

Most PCB congeners are solids at ambient temperature, however Aroclor formulations are viscous liquids of density greater than water, and are resistant to acids, bases and heat. PCBs have low water solubility, which decreases with increasing level of chlorination. For example, the solubility of one of the monochlorinated biphenyls is 5.9 mg/L while that of the decachlorinated biphenyl is only 0.015 mg/L. Vapour pressure and degradability also decrease with increasing chlorination. Vaporization rates for 6 common Aroclors show that the vaporization rates decrease about 200-fold from Aroclor 1221 which consists primarily of mono- and dichlorobiphenyls to 1260

TABLE 1

SELECTED PHYSICAL-CHEMICAL PROPERTIES OF THE POLYCHLORINATED BIPHENYLS (PCBs)

Compound	Cl No.	MW (g)	MP (K)	V (cm /mol) (LeBas)	TSA A	Solubility C(S)	Solubility C(L)	Vapour Pressure P(S)	Vapour Pressure P(L)	log Kow
PCBs Biphenyl	0	154.2	344	184.6	192.2	45.4	129.7	2.43	6.9	3.9
mono-	1	188.7	298.1-350.9	205.5	208.4-210	6.36-29.15	13.24-35.66	0.271-2.04	0.9-2.5	4.3-4.6
di-	2	223.1	297.2-422	226.4	224.2-227.6	0.27-8.96	4.56-10.14	0.0048-0.279	0.008-0.60	4.9-5.3
tri-	3	257.5	317-360	247.3	241.6-243.6	0.06-1.35	0.24-2.39	0.0136-0.143	0.003-0.22	5.5-5.9
tetra-	4	292.0	320-433	268.2	255.6-259.6	0.02-0.342	0.13-1.30	5.9×10^{-5}-.0054	0.002	5.6-6.5
penta-	5	326.4	249.5-397	290.1	269.2-275.2	0.0123-0.06	0.093-0.337	2.04×10^{-7}-0.0093	0.002-0.05	6.2-6.5
hexa-	6	360.9	350-433	310	867.2-291.5	0.0011-0.0026	0.0061-0.02	2×10^{-6}-0.00159	0.0007-.01	6.7-7.3
hepta-	7	395.3	395.4-422	330.9	302.6	0.00114-0.00506	0.0191-0.05	2.73×10^{-5}	0.00025	6.7-7.0
octa-	8	429.8	432-435	351.8	317.9-318.7	0.00047-0.0007	0.0098-0.0150	0.0000266	0.0006	7.1
nona-	9	464.2	455-479	372.7	331.9	0.00003-0.00024	0.00141-0.0146	-	-	7.2-8.16
deca-	10	498.7	578.9	393.6	343.9	0.0000024	0.0144	0.00000005	0.00003	8.26

(Taken from Shiu et al., 1987)

Cl No. Chlorine Number
MW Molecular Weight
MP Melting Point
V Viscosity
TSA Total Surface Area
C(S) Solubility
C(L) Subcooled Liquid Solubility
P(S) Vapour Pressure
P(L) Subcooled Liquid Vapour Pressure
log Kow log Octanol-water Partition Coefficient

TABLE 2

AVERAGE MOLECULAR COMPOSITION (WT.%) OF SEVERAL AROCLORS

No. of Chlorine Atoms	Aroclor						
	1221	1232[a]	1016	1242	1248	1254	1260
0	10						
1	50	26	2	1			
2	35	29	19	13	1		
3	4	24	57	45	2	1	
4	1	15	22	31	49	15	
5				10	27	53	12
6					2	26	42
7						4	38
8							7
9							1

a-Five Percent Unidentified

(Taken from Brinkman and DeKok, 1980.)

TABLE 3

COMPARISON OF COMMERCIAL PCB MIXTURES

TRADE NAMES					
Aroclor[a]	Clophen[b]	Phenoclor[c]	Pyralene[c]	Kanechlor[d]	Fenclor[e]
1221					
1232			2000	200	
			1500		
1242	A30	DP3	3000	300	42
1016					
1248	A40	DP4		400	
1254	A50	DP5		500	54
1260	A60	DP6		600	64
1262					
					70
1268					
1270					
					DK

a Monsanto Industrial Chemicals Co. USA
b Bayer, GFR
c Caffaro, Italy
d Kanegafuchi Chemical Co.,Japan
e Prodelec, France

(Taken from Brinkman and DeKok, 1980)

TABLE 4

CHARACTERISTICS OF AROCLOR MIXTURES

Aroclor	Density (at 20°C)	Viscosity (Saybolt Univ. sec) at 98.9°C	n_D^{20}	Flash Point (°C)	Fire Point (°C)	Pour Point (°C)	Distillation Range (°C)	Vaporization Rate (g/cm /h) X 10^6, at 250°C	Dielectric Constant 20°C	Dielectric Constant 100°C	Solubility in Water at 25°C (ug/L)
1221	1.18	30-31	1.618	141-150	176	1	275-320	1,740			
1232	1.26	31-32	1.621	152-154	238	-35	270-325	874	5.7	4.6	
1016	1.37		1.623	170	ntb		323-356				
1242	1.38	34-35	1.628	176-180	ntb	-19	325-366	338	5.8	4.9	240
1248	1.44	36	1.631	193-196	ntb	-7	340-375	152	5.6	4.6	52
1254	1.54	44-58	1.640	ntb	ntb	10	365-390	53	5.0	4.3	12
1260	1.62	72-78	1.648	ntb	ntb	31	385-420	13	4.3	3.7	3
1262	1.64	86-100	1.651	ntb	ntb	35-38	390-425	9			
1268	1.81			ntb	ntb		435-450		2.5		
1270	1.95			ntb	ntb		450-460				

ntb=none to boiling

(Taken from Brinkman and DeKok , 1980)

which consists essentially of penta-,hexa-, hepta-, and octadichlorobiphenyl. In environmental samples where PCBs are sorbed on soil or sediment surface the site of vaporization of PCBs is greatly reduced. The vaporization rate depends upon the sorption surface, organic matter content, type of clay and pH of the medium. Transport and fate of PCBs in aquatic systems and their partitioning in different compartments of the environment depends to a large degree on the sorption reactions. Generally sorption increases with increase in chlorine content of the chlorobiphenyl, as can been seen with octanol water partition coefficient, and with surface area and organic carbon of the sorbent.

A common product class containing PCBs which is used as an electrical insulating media is askarel. The capacitor askarels include neat Aroclor 1242,1254 and 1016 and a mixture of 75% Aroclor 1254 and 25% trichlorobenzene. The most commonly used transformer askarels are 60% Aroclor 1260/40% trichlorobenzene and 70% Aroclor 1254/30% trichlorobenzene. These transformer askarels may also contain other minor components which are used as free radical scavengers. The ASTM (1983) provides standard specifications for askarels.

The procedure for PCBs analysis can be divided into four sections. These are

SAMPLE COLLECTION AND STORAGE

EXTRACTION

CLEANUP

PCB DETERMINATION TECHNIQUES

Each of these will be discussed individually in the following section.

SAMPLE COLLECTION AND STORAGE

PCBs are an inert, non-polar class of semivolatile organic compounds. With the exception of the air and water sampling techniques which concentrate the PCBs from the matrix onto an adsorbent, most PCB sample collections have utilized the standard methods for semivolatile organics in the subject matrix. In all cases, if the samples are to be analyzed shortly after collection no storage requirements are needed.

A summary of collection and storage methods are listed in Table 5. Erickson (1986) gives a detailed review of these methods.

TABLE 5

SUMMARY OF SAMPLE COLLECTION AND STORAGE TECHNIQUES FOR PCBS

WATER SAMPLES

1. GRAB SAMPLING
   - -most common procedure
   - -collected in glass containers
   - -iced or refrigerated from the time of collection until extraction

2. AUTOMATIC COMPOSITE SAMPLING
   - -consists of a pump, tubing, a timer and a collection vessel

3. SOLID ADSORBENT SAMPLING
   - -preconcentrate PCBs from a large volume of water onto a small volume of solid adsorbent which may be easily transported, stored and extracted
   - -preconcentration can enhance the method detection limit
   - -solid adsorbent-polyurethane foam,macroreticular resin, tenax

4. LIQUID-LIQUID EXTRACTION SAMPLING

AIR SAMPLES

1. SOLID ADSORBENT SAMPLING
   - -solid adsorbent-polyurethane foam, Florisil,XAD-2

2. LIQUID SORBENT SAMPLING
   - - a wide variety of glassware geometries and liquids ranging in volatility from hexane to ethylene glycol have been used

SOLIDS SAMPLES

TRACE ORGANIC SAMPLING
- -soil, sediment, biota and tissue sampling for PCBs all utilize general trace organic sampling techniques
- -sampling equipment and containers must be glass, steel, TFE or other non-contaminated materials
- -samples collected must be representative of the system and the sample volume must be sufficent for the analyst's need

SURFACE SAMPLES

No standard surface sampling technique has been issued by an organization.

NONPOROUS SURFACES

EPA guidance document on PCB spill cleanup recommends that nonporous surfaces be sampled by wiping with a moistened piece (e.g. with toluene, isooctane,etc.) of filter paper. The paper is held with a pair of stainless steel forceps and an area 100 cm of the surface be sampled. The paper should be stored at 4°C in a precleaned glass jar. This method should be reproducible.

POROUS SURFACES

-should be sampled by physical removal of a representative portion

OIL SAMPLES

GRAB SAMPLING OF REPRESENTATIVE SAMPLE (homogeneous)

EXTRACTION

Since PCBs are nonpolar , semivolatile organics, they are highly soluble in nonpolar solvents (e.g. hexane) and only slightly soluble in polar solvents (e.g. water and acetonitrile). This property is advantageous for extraction from water samples, however for PCBs in nonpolar matrix the extraction process becomes much more difficult.

A summary of the extraction methods are given in Table 6 . Erickson (1986) gives a detailed review of these methods.

TABLE 6

SUMMARY OF EXTRACTION TECHNIQUES FOR PCBS

WATER SAMPLES

1. LIQUID-LIQUID EXTRACTION
   -straightforward since solubility is so low
   -solvents used hexane/CH CL,CH CL ,H O/CH CN/hexane,hexane/CH CL /acetone,hexane/acetone,CH CN,hexane/ether,pentane, pentane/methanol,petroleum ether/CH CN,isooctane
   -extraction followed by KOH saponification technique

2. CONTINUOUS LIQUID-LIQUID EXTRACTION

3. STEAM DISTILLATION TECHNIQUE

4. SORBENT COLUMN EXTRACTION

5. PURGE AND TRAP

SEWAGE/SLUDGE SAMPLES

1. SOLVENT EXTRACTION
   -critical component of the extraction technique is the contact between the solvent and the matrix
   -can be accomplished by physical wetting and use of "wetting" solvent mixture
   -viscous samples can be treated by diluting the matrix to the desired consistency

2. SORBENT COLUMN EXTRACTION
   -column of polyvinyl chloride chips gives best result

3. CENTRIFUGE METHOD
   -acetone/CH CH/hexane mixture and then centrifuged to separate the emulsified mixture

4. COLUMN ELUTION
   -sludge is mixed with anhydrous sodium sulfate and then packed into a HPLC column, eluted with acetone/hexane

5. SOXHLET EXTRACTION
   -sludge is mixed with anhydrous sodium sulfate and then Soxhlet extracted with CH CL /hexane

6. CONTINUOUS LIQUID-LIQUID EXTRACTION

SEDIMENT/SOIL SAMPLES

1. SOLVENT EXTRACTION
   -mixing and pulverizing of chunks is an important preextraction step
   -sediment is centrifuged to remove excess water,wetted with acetone,extracted with hexane, rewetted with acetone and

extracted again with hexane, shaken each time on a wrist-action shaker
-other wetting solvents are acetonitrile or water/acetonitrile
-ultrasonic, Soxhlet, blender and shake methods
-steam distillation
-examples of solvents used-
acetone/hexane,water/methanol/hexane,pentane,petroleum ether dichloromethane

2. THERMAL DESORPTION

AIR SAMPLES

-sorbent matrices (e.g. polyurethane foam,Florisil, XAD-2) are extracted with repeated extraction with a nonpolar solvent (hexane,benzene or methylene chloride)

OIL SAMPLES

1. SIMPLE DILUTION OF MATRIX
-hexane dilution has been shown to be the best methods

2. LIQUID-LIQUID EXTRACTION
-acetonitrile/hexane

SILICONE OILS SAMPLES

1. ACETONITRILE PARTITIONING

2. CARBON COLUMN EXTRACTION

CLEANUP

The cleanup step in an analytical procedure removes other compounds which may interfere with the determination of PCBs. It takes advantage of the difference in physical or chemical properties of PCBs and interferences. The extent of cleanup required is dependent on the requirements of the determination step.

A summary of the cleanup methods are given in Table 7 . Erickson (1986) gives a more detailed review of these methods.

TABLE 7

CLEANUP TECHNIQUES FOR PCBS

ADSORBENT COLUMN CHROMATOGRAPHY
Florisil, silica gel, carbon or alumina

with

ethyl ether/petroleum ether or ethyl ether/hexane or dichloromethane/hexane or methanol/hexane

ADSORPTION COLUMN CHROMATOGRAPHIC FRACTIONATION TECHNIQUES

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

ADSORBENT SLURRY TECHNIQUE

THIN LAYER CHROMATOGRAPHY

GEL PERMEATION CHROMATOGRAPHY

LIQUID-LIQUID PARTITIONING

CHEMICAL DEGRADATION WITH ACID OR BASE
sulfuric acid and chromium trioxide

PCB DETERMINATION TECHNIQUES

A wide variety of instrumental techniques are available to determine the PCB content of a sample. A summary of these techniques are listed in Table 8.

The choice of determination technique depends upon a number of factors e.g.

sample preparation and cleanup
extraction procedure
limit of detection required
resolution required
interferences
quantitative accuracy and precision
availability of instrumentation
analysis time and cost
portability of instrumentation
degree of interpretation of results.

For field portable techniques one sacrifices the confidence in the analysis for speed and/or simplicity of apparatus. Many of these techniques provide only qualitative or semiquantitative information.

Currently, PCB determination techniques which have been and are being developed for field use are

Thin layer chromatography
Gas chromatography with electron capture detector
X-ray fluorescence
Chemical determination of total chloride
Fourier transform infrared spectrometer
Mass spectrometer

Only the thin layer chromatography and the chemical determination of total chloride can be considered as person portable systems due to the weight factor Each of these techniques will be discussed in the following section.

PERSON PORTABLE ANALYTICAL SYSTEM

THIN LAYER CHROMATOGRAPHY (TLC)

Since the publication of a TLC qualitative method for PCBs by Mulhern (1968) and Mulhern et al.(1972), several researchers have used TLC to analysis for PCBs in various matrices. Methods have been described by Willis and Addison (1972) and Stalling and Huckins (1973) for the analysis of Aroclor mixtures; by Piechaluk (1984) for the analysis of PCBs in soil and by Stahr (1984) for the analysis of oils containing PCBs. Use of TLC for on location qualitative analysis of PCBs at spills has been

TABLE 8

SUMMARY OF PCBS DETERMINATION TECHNIQUES

A. CHROMATOGRAPHIC TECHNIQUES

1. GAS CHROMATOGRAPHY (GC)

Separation -packed column gas chromatography
-high resolution gas chromatography

Detection -electron capture detection (ECD)
-Hall electrolytic conductivity
-mass spectrometry
electron impact mass spectrometry
positive chemical ionization mass spectrometry
negative chemical ionization mass spectrometry
high resolution electron impact mass spectrometry
mass spectrometry/mass spectrometry
-flame ionization detection
-photoionization
-thermal conductivity

2. THIN-LAYER CHROMATOGRAPHY

3. LIQUID CHROMATOGRAPHY Adsorption liquid solid chromatography
Reversed-phase liquid chromatography

4. PLASMA CHROMATOGRAPHY

B. NONCHROMATOGRAPHIC METHODS

1. NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

2. INFRARED SPECTROMETRY

3. RADIOIMMUNOASSAY

4. INTERRUPTED-SWEEP VOLTAMETRY

5. LOW TEMPERATURE LUMINESCENCE

6. NEUTRON ACTIVATION ANALYSIS

7. CHEMICAL DETERMINATION OF TOTAL CHLORIDE

8. CHEMICAL DETERMINATION OF TOTAL CHLORINATED ORGANICS

9. X-RAY FLUORESCENCE

reported by Ponton (1986) and Holtz and Sharpe (1986). Problems were encountered with portable field testing kits at temperatures less than 0°C. TLC has been shown to be an effective technique for determining PCBs in a variety of contaminated matrix. The advantages of it include its ease of use, rapid analysis and the simplicity of the apparatus. The disadvantages include lack of resolution, moderate sensitivity and low specificity. A more detailed review of this technique is given by Erickson (1986). Mulhern (1968) has also used this method in conjunction with GC/EC for qualitative confirmmation of results.

CHEMICAL DETERMINATION OF TOTAL CHLORIDE

These chemical determination methods are based on stripping the chlorine off the PCBs and measuring the resultant chloride ions by several different means.

A review of each will be presented in the following section. It will not be restricted to only the person portable analytical systems.

REACTIONS FOR REMOVAL OF CHLORINE FROM PCBS

Wet Reduction

The chlorine atom can be stripped off the PCBs by using metallic sodium or organo-sodium reagents. Examples of organo-sodium reagents are

-sodium naphthalide reagent. This reagent is prepared by heating metallic sodium to 150-170 °C in an inert atmosphere, cooling the mixture and adding a solution of tetrahydrofuran and naphthalene. The reagent is added to PCB contaminated oil at a 1:50 or 1:100 mole ratio (Goodyear,1980).

-Acurex reagent. This reagent is similar to the sodium naphthalide reagent with one modification. The naphthalene is replaced with another compound (Acurex, 1983).

-sodium polyethylene glycol complex. Various molecular weights of polyethylene glycol may be combined with metallic sodium to form the reagent. This reagent is made by drying polyethylene glycol over anhydrous sodium sulfate and adding it to metallic sodium (Ackerman et al., 1983). Then this mixture is added to PCB contaminated oil on a batch basis.

Reilly (1960) also reported on the reduction and fusion of the halides from the organic complexes with magnesium, lithium or potassium. These methods require high temperatures with elemental potassium.

PCBs in transformer oils react with polyethylene glycols and potassium hydroxide . The products of this reaction are polyglycols,polychlorobiphenyl alcohols and salts. Adams and Peterson (1985) have used dimethylsulfoxide as a co-solvent to improve the rate of extraction in this process.

Catalytic dehydrochlorination employs ethanolic sodium

hydroxide and hydrogen in a reaction vessel under 3-5 MPa. The catalyst is 10% palladium on charcoal or 61% nickel on kieselguhr. Reaction products consist of hydrocarbons, incompletely dechlorinated materials, salts and water

Dry Reduction

The dry technique for reduction uses a 950° C furnace and molecular hydrogen.

Dry Oxidation

Dry oxidation is one of the methods for total halide concentration. There are two basic techniques: the Oxygen Furnace (Agazzi et al., 1958) which has been applied only to oils contaminated with pesticides and the Schoniger Flask (Lisk, 1960). The extract is burned in oxygen at ambient pressure using a standard quick-fit flask. The resulting chlorine is absorbed in water or base in the flask for subsequent determination by a variety of methods which will be discussed in the next section. Interferences are minimal since all organic materials burn to carbon dioxide and sulfur compounds to sulfur dioxide.

Wet Oxidation

A common wet oxidation procedure for organic halides is the Carius technique (Steyermark, 1961). The technique uses nitric acid and a combustion furnace to oxidize the organohalogen in the presence of silver nitrate to form a silver halide.

The Parr bomb which uses peroxide in a pressurized combustion method is another wet oxidation method.

A wet oxidation technique of some interest is that reported by Judah (1948) using sulfuric acid and silver dichromate in a distillation reaction at atmospheric pressure and at 110°C.

MEASUREMENT OF THE RESULTANT CHLORIDE IONS

Through the determination of chloride, the investigator can calculate the amount of PCBs in a sample based on the percentage weight of chlorine in the various Aroclors. Methods for the determination of chloride are reviewed in the following section.

Argentometric Method

The argentometric principle is based on the silver nitrate titration of chloride. In a neutral or slightly alkaline solution, potassium chromate acts as an indicator for the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (Standard Methods, 1975).

Mercuric Nitrate Method

Chloride can be titrated with mercuric nitrate due to the formation of soluble mercuric chloride. In the pH range 2.3 to 2.8, s-diphenylcarbazone indicates an endpoint of the titration by the formation of a purple complex with excess mercuric ions. A second indicator, alcoholic xylene cyanol is used as a pH indicator and may be used for endpoint determination (Standard Methods, 1975).

Potentiometric Methods

Chloride is determined by potentiometric titration with a silver nitrate solution and a glass and silver chloride electrode system. A voltmeter or pH meter is incorporated between the two electrodes. The end point of the titration is that reading which is the greatest change in voltage for a small increment of silver nitrate added (Standard Methods, 1975).

The use of a chloride specific ion electrode is another example of a potentiometric method. No titration of chloride is required, although the electrode must be calibrated for use against standard chloride solutions.

Mercury (II) Chloranilate Method

The mercury (II) salt of chloranilic acid (2,5-dichloro-3,6-dihydroxy-p-benzoquinone) may be used for the determination of small amounts of chloride. The reaction is

$$HgC_6Cl_2O_4 + 2\ Cl^- + H^+ \rightleftharpoons HgCl_2 + HC_6Cl_2O^-$$

The amount of reddish-purple acid chloranilate ion liberated is proportional to the chloride ion concentration. Measurements are made at 530 nm or 305 nm (Vogel,1978).

Mercury (II) Thiocyanate Method

This method is based on the displacement of the thiocyanate ion from mercury (II) thiocyanate by the chloride ion in the presence of the iron (III) ion. A highly colored iron (III) thiocyanate complex is formed and the intensity of the colour is proportional to the original chloride ion concentration. The reaction is

$$2Cl^- + Hg(SCN)_2 + 2Fe^{+3} \rightleftharpoons HgCl_2 + 2(Fe(SCN))^{+2}$$

Measurements are made at 460 nm (Vogel,1978).

COMMERCIALLY AVAILABLE PERSON PORTABLE KITS

Person portable kits are commercially available which determine chloride by measurement with chloride electrode and by colorimetric means. These methods have relatively fast analysis times (less than 20 minutes) and require no sample preparation. They determine the chlorine/chloride content present. If separation from other chlorinated compounds (e.g. trichlorobenzene) is not part of the procedure, then these methods will lead to errors in the determination of PCB content. In addition, differences in the average chlorine content for the various Aroclor mixtures further introduces inherent errors because of average molecular weights, even when correction for or elimination of the trichlorobenzene interferences are made. However this can be overcome if the Aroclor is known.

Examples of the various means of determination are presented in this section.

Free chloride ion can be detected by a chloride ion-specific electrode or colorimetrically. Examples of the colorimetric methods are

Kwik Skrene PCB Test Kit
Clor-N-Oil

An example of the ion-specific electrode is the McGraw Edison PCB Field Test Kit.

KWIK SKRENE PCB TEST KIT

The Kwik Skrene PCB test kit is based on the chemical removal of chlorine atom(s) from the parent biphenyl group. Sodium biphenyl in solvent is the reagent used to break the carbon-chlorine bonds. An oxidizer,potassium persulfate, thymol red and mercuric salts are used for the colorimetric determination of chloride ions (Valin,1986). Standards are incorporated into the kit and PCB concentrations are determined to be greater or less than 35 ppm or 50 ppm or 10 ppm, based on the colour formed. Yellow indicates a concentration less than 50 or 35 ppm of PCBs and blue a concentration greater. Analysis time is approximately 35 minutes.

The Kwik Skrene PCB test kit is for the determination of contaminated oils and soils. The test kit is non-specific in regards to identifying Aroclor types. Other chlorinated aromatics, such as trichlorobenzenes will interfere with the chemical reaction and increase the final PCB concentration.

This kit is person portable and weighs approximately 5 kg for the oils. The soil kit uses an extraction agent and efficient shaking, followed by simultaneous clarification and filtration to prepare an oil/PCB extract from a soil sample for detection of PCBs. An oven is also recommended to dry the samples. The weight of this kit is approximately 40 kg. This system can be put in the back of a station wagon.

The Kwik Skrene PCB test kit was initially developed by British Columbia Hydro, and subsequently the rights were licensed by Syprotec Incorporated, Pointe Claire, Quebec. The kit is solely distributed in Canada by Syprotec Inc.

CLOR-N-OIL

The Clor-N-Oil kit developed for the Electric Power Research Institute and marketed by Dexsil Corporation is based on the quantitative conversion of the chlorine atoms on PCBs to chloride ions which in turn are extracted into an aqueous solution and measured colorimetrically. Chlorine is converted to chloride ions by sodium salts formed by naphthalene together with the dimethyl ether of diethylene glycol as the stabilizing lignand. The chloride ions are extracted into an aqueous buffer solution and reacted with a carefully controlled amount of dissolved mercuric nitrate. Diphenylcarbazone is added. Reaction of any excess mercuric ion with the diphenylcarbazone will form a vivid blue complex. If the chloride ion content exceeds that taken up by the available mercuric ion, the complex is not formed and the reaction mixture remains colorless to pale yellow. The reactions are carried out in soft plastic test tubes containing premeasured reagents in breakable glass ampules. Proper control of the sample size and of the quantity of mercuric nitrate allows the blue-colourless response level in the mineral transformer oil to be set at levels from a few ppm to several thousand ppm. Analysis time is approximately ten minutes.

The lowest ratio of chlorine to PCB found in an askarel is 0.42 (Aroclor 1242). Therefore, an oil sample containing less than 21 ppm chlorine can not contain more than 50 ppm PCB. A colour response level set at 21 ppm chlorine for the kit should assure that no contaminated oil (i.e. 50-500 ppm) gives blue responses.

Individually packaged kits contain reagents in crushable glass ampules. The ampules are sequentially broken and the final colour indicates PCB content. Two kits are presently available, 0-50 ppm and 0-500 ppm PCB content. Each kit allows the investigator to perform one test.

The Clor-N-Oil PCB screening kit is limited in application to contaminated oils. This kit is non-specific in regards to identifying Aroclor types. Other chlorinated aromatics such as trichlorobenzene will interfere with the chemical reaction and increase the final PCB concentration.

The kit weighs 60 grams. It is marketed and distributed in Canada by Nedco, Mississauga,Ontario.

MCGRAW-EDISON PCB FIELD TEST KIT

The portable McGraw-Edison kit provides the necessary hardware, chemical reagents and standard solutions to perform fifty separate tests on PCB contaminated soils or oils. It weighs approximately 7 kg. The kit is based on the quantitative conversion of the chlorine atoms in PCB contaminated materials to chloride ions which in turn are measured by a chloride ion specific electrode. The electrode must be continuously calibrated when it is in use. Names of the chemical reagents used in this kit are not given.

The reported range of detection for Aroclor 1242 is 13-1815 ppm and for Aroclor 1260 6-1046 ppm, in both contaminated soils and oils (Sullivan,1986; Debellefeuille, 1985). This kit is non-

specific in regards to identifying Aroclor types. Other chlorinated aromatic compounds will interfere.

The McGraw-Edison PCB field test kit was developed and originally marketed by Centec Analytical Services Division of Centec Corporation, Virginia and later purchased by McGraw-Edison, Wisconsin. This kit is marketed in Canada by McGraw-Edison Limited, Scarborough, Ontario.

CHEMICAL DETERMINATION OF TOTAL CHLORINATED ORGANIC COMPOUNDS

Two techniques for total chlorinated organics involve concentration of the organic halides on a sorbent trap, and reduction to HCl at 950°C. In one system the HCl gas is detected by electrolytic conductivity (Model 610 Total Organic Halogen Analyzer, O.I. Corporation, College Station, Texas). In the other system, the HCl gas is detected by microcoulometry (Model DX-20 Total Organic Halide Analyzer, Dohrmann Xertex, Santa Clara, California). Both techniques have the advantage over previously used methods in that volatile, semivolatile and non-volatile organic chlorides can be detected. The electrolytic conductivity technique was characterized by Bernard and Russell (1983). The analyses with the electrolytic conductivity technique are quite rapid and reproducible. The response is linear with concentration. The microcoulometric technique was characterized by Berger (1984).

SELECTION, EVALUATION, MODIFICATION AND RECOMMENDATION OF METHODOLOGY FOR PCB ANALYSIS IN A PERSON PORTABLE ANALYTICAL SYSTEM

Following the review of the methods in the literature for

PCB Sample Collection and Storage

PCB Extraction

PCB Cleanup

PCB Determination Techniques

a choice of one from each of these areas was made for application within the kit. This was followed by an evaluation, in some cases, a modification and finally a recommendation. The criteria for selection was based on the Level 2 systems.

SAMPLE COLLECTION

SELECTION OF SAMPLING TECHNIQUES

The types of media to be sampled can include soil, water and solid surfaces (e.g. concrete, asphalt wood, etc.). General sampling methods are described in the following section. These methods were taken from EPA (1985).

Solid sampling

When soil, sand or sediment samples are to be taken, a surface scrape sample of approximately 1 cm should be collected with a trowel or similar implement, preferably stainless steel. The sample should be scraped directly into a precleaned glass bottle and weighed. If it is free flowing, the sample should be thoroughly homogenized by shaking. If not, the sample should be mixed to create a representative sub-sample. For samples, such as sod, core samples not more than 5 cm deep should be taken using a soil coring device. Before collection of verification samples, the equipment should be used to generate a field blank.

Water Sampling

Surface Sampling

If PCBs dissolved in a hydrocarbon oil are spilled, they will most likely be dispersed on the surface. Therefore, a surface water collection technique must be used. Surface water samples should be collected by grab techniques. When appropriate, the precleaned glass sample bottle may be dipped directly into the body of water at the designated sample collection point. A sample is collected from the water surface by gently lowering a

precleaned sample bottle horizontally into the water until water begins to run into it. The bottle is then slowly turned upright keeping the lip just under the surface so that the entire sample is collected from the surface.

Subsurface Sampling

If the PCBs are in an Askarel or other heavier-than-water matrix, the PCBs will sink. In these cases water near the bottom should be collected. To collect subsurface water, the bottle should be lowered to the specified depth with the cap on. The cap is then removed, the bottle allowed to fill, and the bottle brought to the surface.

Other Sampling Approaches

When the above approaches are not feasible, other dippers, tubes, siphons, pumps, etc., may be used to transfer the water to sample bottle. The sampling system should be of stainless steel, Teflon, or other inert, impervious and noncontaminated material. Before collection of samples, this equipment must be used to generate a field blank.

Surface Sampling

Wipe Sampling

Smooth and impervious surfaces should be sampled by first applying an appropriate solvent (e.g. hexane) to a piece of 11 cm filter paper (e.g. Whatman 40 ashless, Whatman "50" smear tabs, or equivalent) or gauze pad. This moistened filter paper or gauze pad is held with a pair of stainless steel forceps and used to thoroughly swab a 100 cm area as measured by a sampling template. Before collection of verification samples, the selected filter paper or gauze pad and solvent should be used to generate a field blank.

Sampling Porous Surfaces

Wipe sampling is inappropriate for surfaces which are porous and would absorb PCBs. These include wood and asphalt. Where possible, a discrete object (e.g., a paving brick) may be removed. Otherwise, chisels, drills, saws, etc., may be used to remove a sufficient sample for analysis. Samples less than 1 cm deep on the surface most likely to be contaminated with PCBs should be collected.

Vegetation Sampling

The sample design or visual inspection may indicate that samples of vegetation (such as leaves, bushes and flowers) are required. In this case, samples may be taken with pruning shears,a saw or other suitable tool and placed in a precleaned glass bottle.

EVALUATION/MODIFICATION OF SAMPLING TECHNIQUES

No evaluation/modification was deemed necessary.

RECOMMENDATION FOR SAMPLING TECHNIQUES

The sampling techniques should be the same as the EPA methods.

STORAGE

SELECTION OF STORAGE TECHNIQUES

If the samples are to be used shortly after collection, as would occur in an on-scene person portable analytical system, no storage requirements should be needed.

EVALUATION/MODIFICATION OF STORAGE TECHNIQUES

No evaluation/modification was deemed necessary.

RECOMMENDATION FOR STORAGE TECHNIQUES

No storage requirements should be needed.

EXTRACTION

SELECTION OF OIL EXTRACTION TECHNIQUES

Simple dilution of transformer oils, capacitors fluids, hydraulic fluids and other oils with pesticide-grade hexane has been shown to be the best method for extraction (Erickson,1986). Thus, oil samples should be extracted with pesticide-grade hexane.

EVALUATION/MODIFICATION OF OIL EXTRACTION TECHNIQUES

The concentrations of several samples of different PCB transformer oils containing Aroclor 1260 (diluted with hexane and neat) were determined by two different methods. These methods were by "wet" test chemistry determination and by a gas chromatography (GC) determination. The wet test chemistry determination are described in the proceeding section. The GC determinations were with a Perkin-Elmer Sigma 2000 GC equipped with a electron capture detector, a 30 meter DB-5 Megabore column. The GC oven was temperature programmed from 50 to 220° at a rate of 10° / minute.

Results are listed in Table 9.

RECOMMENDATION

The oil samples should be extracted with pesticide-grade hexane.

TABLE 9

PCBs CONCENTRATIONS OF AROCLOR 1260 SAMPLES NEAT AND DILUTED WITH PESTICIDE-GRADE HEXANE

Sample No.	Concentration of Aroclor 1260 determined by Chloride Determination	Concentration of Aroclor 1260 determined by GC/ECD
84	2992 2945	4445
85	10110 12500 11340	20088
86	14660 11095 14600	35600
X 10 Dilution with Pesticide Grade Hexane		
84	703	400
85	1522 1690 1521 1475	1800
86	2383 1928 2655 2645	3200
X 100 Dilution with Pesticide Grade Hexane		
85	279 400 300	180
86	493	320

SELECTION OF SOIL EXTRACTION TECHNIQUES

A wide variety of procedures have been described in the literature for the extraction of PCBs from soil and sediment (Erickson,1986) as previously discussed. These procedures have involved solvents such as hexane, acetone,acetonitrile,pentane,petroleum ether and dichloromethane. Pesticide-grade pentane and HPLC grade hexane should be used for soil extraction.

EVALUATION/MODIFICATION OF SOIL EXTRACTION TECHNIQUES

The effects of total organic carbon (TOC) content on PCB extracted with hexane from soil were also investigated in this evaluation. Three soil types were selected:

potting soil-with an organic carbon content of 12-14%, as determined by a previous study
-rich in humic acid

clay soil -3-4% organic carbon

sand -0.5% organic carbon or less

Procedures for Evaluation

1. Soils were spiked with known amounts and known concentrations of PCBs contaminated transformer oils.

2. 10 grams of homogeneous mixed, sieved soil samples were weighed and placed in 125 mL Erlynmeyer flask.

3. 25 mL of solvent were added to the flasks. The contents were swirled.

4. The contents of the flasks were filtered with Whatman #42 paper filters into 150 mL beakers

5. Steps 3 and 4 were repeated until a total volume of 100 mL of solvent was used.

6. Using low heat on a portable hot plate or on the small Cook-It stove from the Hach Kit the solvent mixtures were concentrated to 10 mL.

7. The solvent mixtures were then transferred to separatory flasks and the procedure was continued as for the transformer oils.

8. Blanks using uncontaminated soils from the same areas as the contaminated samples were also determined.

Listed in Tables 10 and 11 are data on PCB contaminated soils using hexane and pentane, as extraction solvents respectively.

TABLE 10

PCB CONTAMINATED SOILS

Extraction Solvent : Pesticide Grade Pentane

Sample No.	Concentration of Chloride (ug/kg)	Concentration of Aroclor 1260 (ug/kg)	Initial Concentration of Aroclor 1260 (ug/kg)	% of Recovered PCBs	Modified Concentration hexane pentane Method 1		Modified Concentration hexane pentane Method 2 (ug/kg)		Modified Concentration hexane pentane Method 3	
Soil Type : 0.5% organic carbon										
85 (1:10)	985	1640	1800	91	1842	1798	1874	1905	1902	1624
86 (1:100)	214	356	356	100	441	372	385	403	391	352
85 (1:100)	130	217	201	> 100	290	218	223	241	238	215
26	51.6	86	83	> 100	147	73	71	87	95	85
86 (1:100)	22.2	37	35.6	> 100	93	18	15	30	41	37
Soil Type : 3-4% Organic Carbon										
85 (1:10)	903	1505	1800	84	1619	1791	1717	1748	1420	1584
86 (1:100)	206	344	356	97	286	386	371	389	325	362
85 (1:100)	123	205	201	> 100	126	218	209	226	193	216
26	48.5	80.9	83	97.5	-16	68	65	81	76	85
86 (1:1000)	20.4	34	35.6	95.5	-70	11.1	11	26	32	36
Soil Type : 12-14% organic carbon										
85 (1:10)	884	1472	1800	82	1890	1803	1679	1709	1654	1752
86 (1:100)	152	254	356	71	222	317	266	284	285	302
85 (1:100)	97	162	201	81	95.7	205	159	176	182	193

26	47	78.4	83	94.5	-18.7	102.5	63	78	88	93
86 (1:1000)	19.2	32	35.6	90	-82.4	45.9	8.7	24	36	38

FIGURE 2

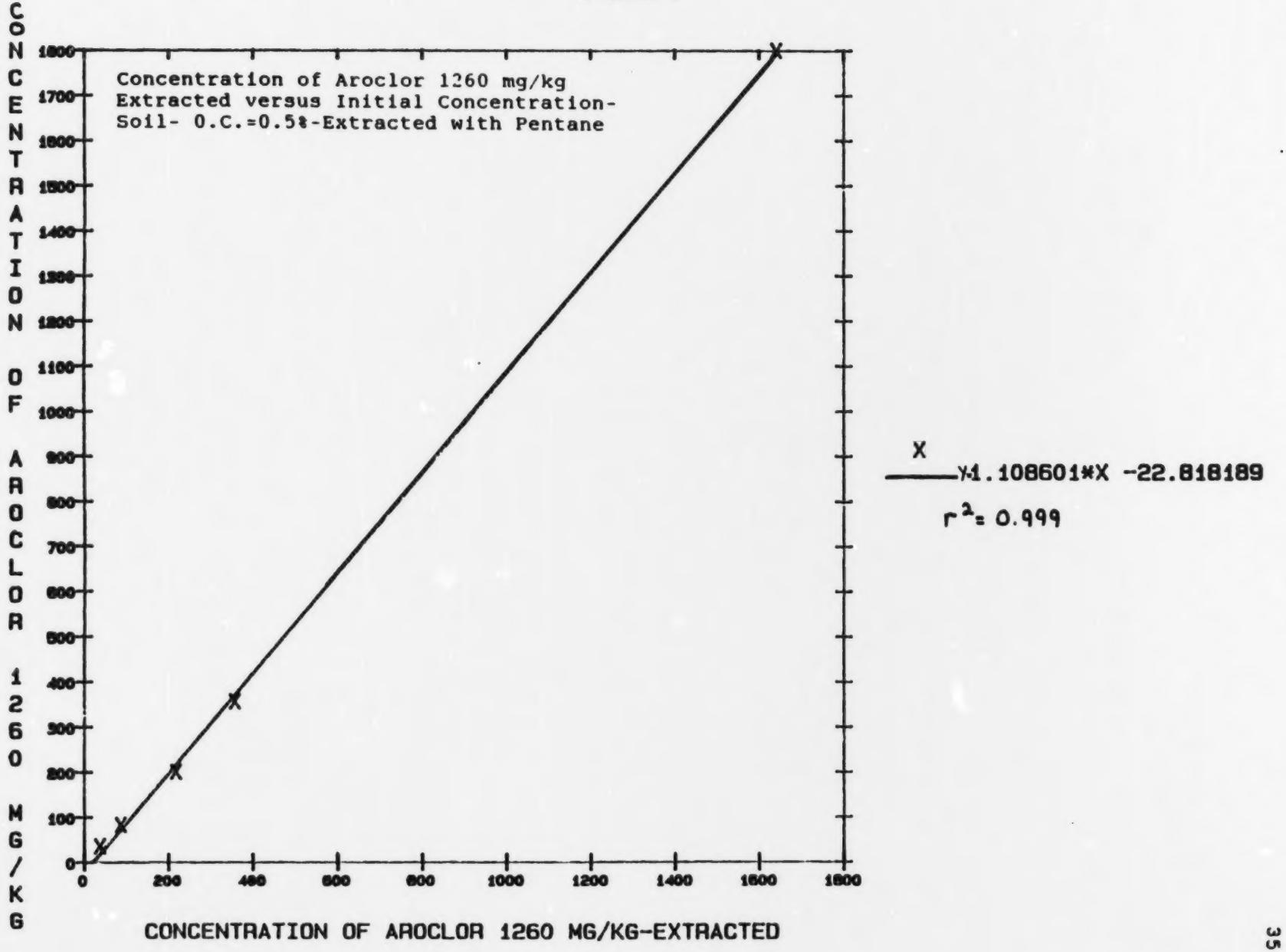
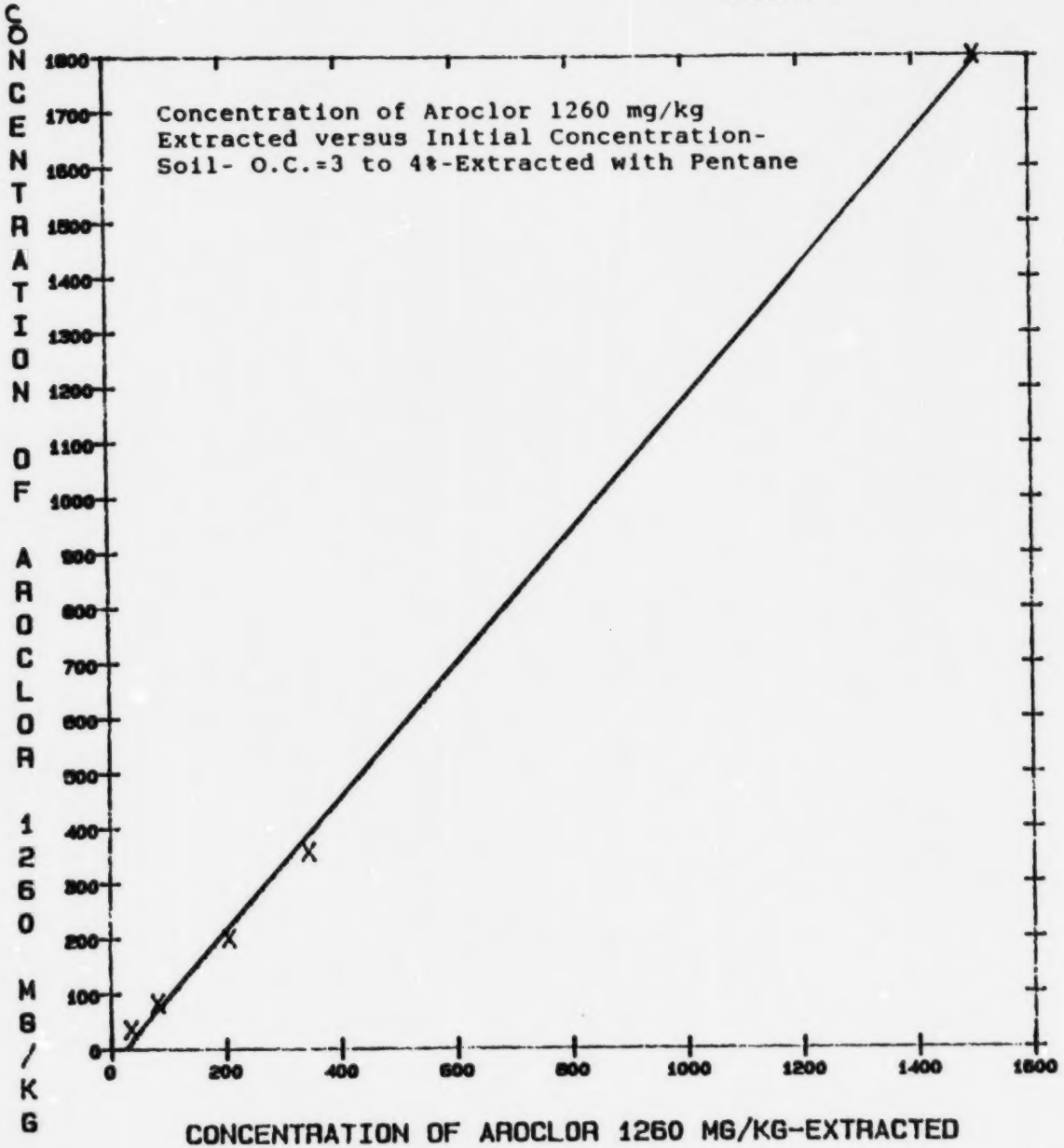

Concentration of Aroclor 1260 mg/kg
Extracted versus Initial Concentration-
Soil- O.C.=0.5%-Extracted with Pentane
CONCENTRATION OF AROCLOR 1260 MG/KG
CONCENTRATION OF AROCLOR 1260 MG/KG-EXTRACTED
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
0
200
400
600
800
1000
1200
1400
1600
1800
X
Y=1.108601*X -22.818189
r^2= 0.999

FIGURE 3



X

X=1.210732*X -30.071252

$r^2 = 0.999$

FIGURE 4

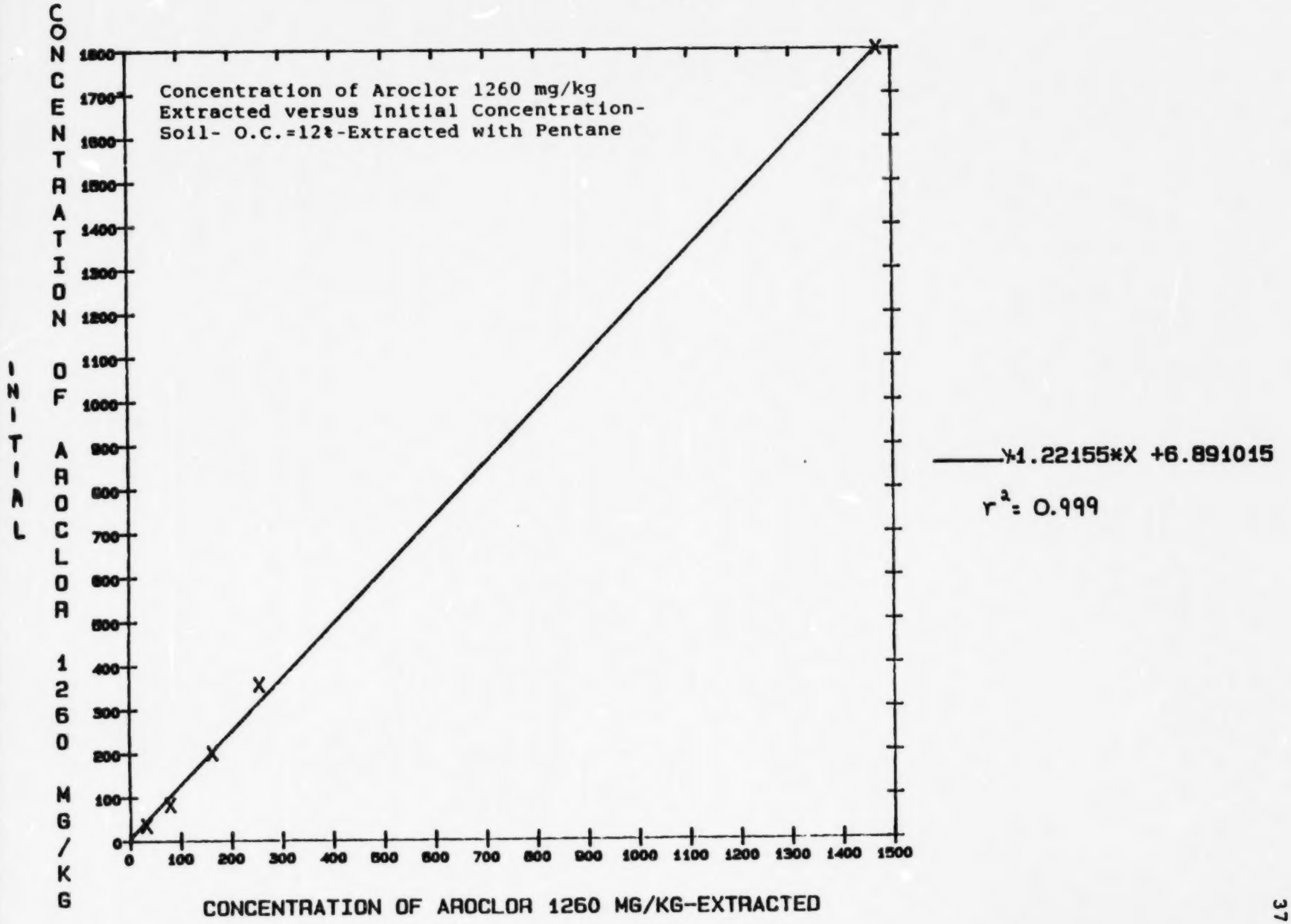

Concentration of Aroclor 1260 mg/kg
Extracted versus Initial Concentration-
Soil- O.C.=12%-Extracted with Pentane
INITIAL CONCENTRATION OF AROCLOR 1260 MG/KG
CONCENTRATION OF AROCLOR 1260 MG/KG-EXTRACTED
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Y=1.22155*X +6.891015
r²= 0.999

TABLE II

PCB CONTAMINATED SOILS

Extraction Solvent : Pesticide Grade Pentane

Sample No.	Concentration of Chloride (ug/kg)	Concentration of Aroclor 1260 (ug/kg)	Initial Concentration of Aroclor 1260 (ug/kg)	% of Recovered PCBs	Modified Concentration hexane pentane Method 1		Modified Concentration hexane pentane Method 2 (ug/kg)		Modified Concentration hexane pentane Method 3	
Soil Type : 0.5% organic carbon										
B6 (1:10)	1832	3050	3200	95	3380	3363	3510	3555	3352	3020
B5 (1:10)	846	1410	1800	78	1591	1542	1607	1636	1549	1396
	843	1405		78	1586	1537	1601	1630	1544	1391
	945	1575		87	1771	1725	1799	1829	1731	1559
B4 (1:10)	302	504	445	>100	603	537	556	576	554	499
B5 (1:100)	119	198	210	94	269	197	201	218	218	196
26	48.3	80.4	83	97	141	66	64.8	80.7	88	79.6
Soil Type : 3-4% organic carbon										
B6 (1:10)	1723	2873	3200	90	3189	3446	3304	3348	2710	3024
B4 (1:10)	337	563	445	>100	537	651	625	645	531	593
B5 (1:100)	120	201	201	100	122	213	205	222	190	212
Soil Type :12-14% organic carbon										
B6 (1:10)	1445	2410	3200	75	3176	2947	2767	2806	2708	2869
B4 (1:10)	311	519	445	>100	585	640	574	594	583	618
B5 (1:100)	92	153	201	76	83.4	194	149	166	172	182

FIGURE 5

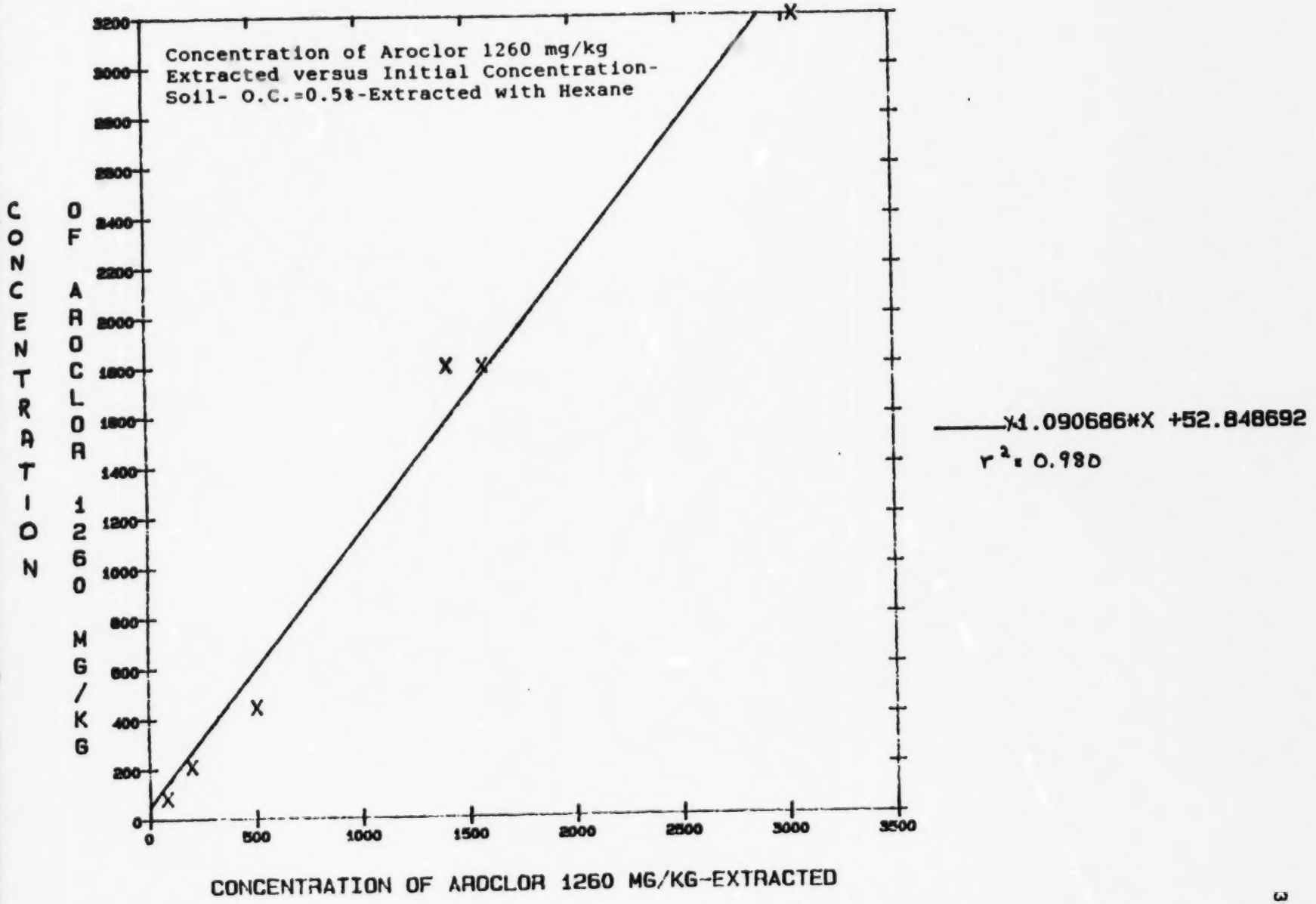

Concentration of Aroclor 1260 mg/kg
Extracted versus Initial Concentration-
Soil- O.C.=0.5%-Extracted with Hexane
CONCENTRATION OF AROCLOR 1260 MG/KG
CONCENTRATION OF AROCLOR 1260 MG/KG-EXTRACTED
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2800
3000
3200
0
500
1000
1500
2000
2500
3000
3500
Y=1.090686*X +52.848692
r²= 0.980

FIGURE 6

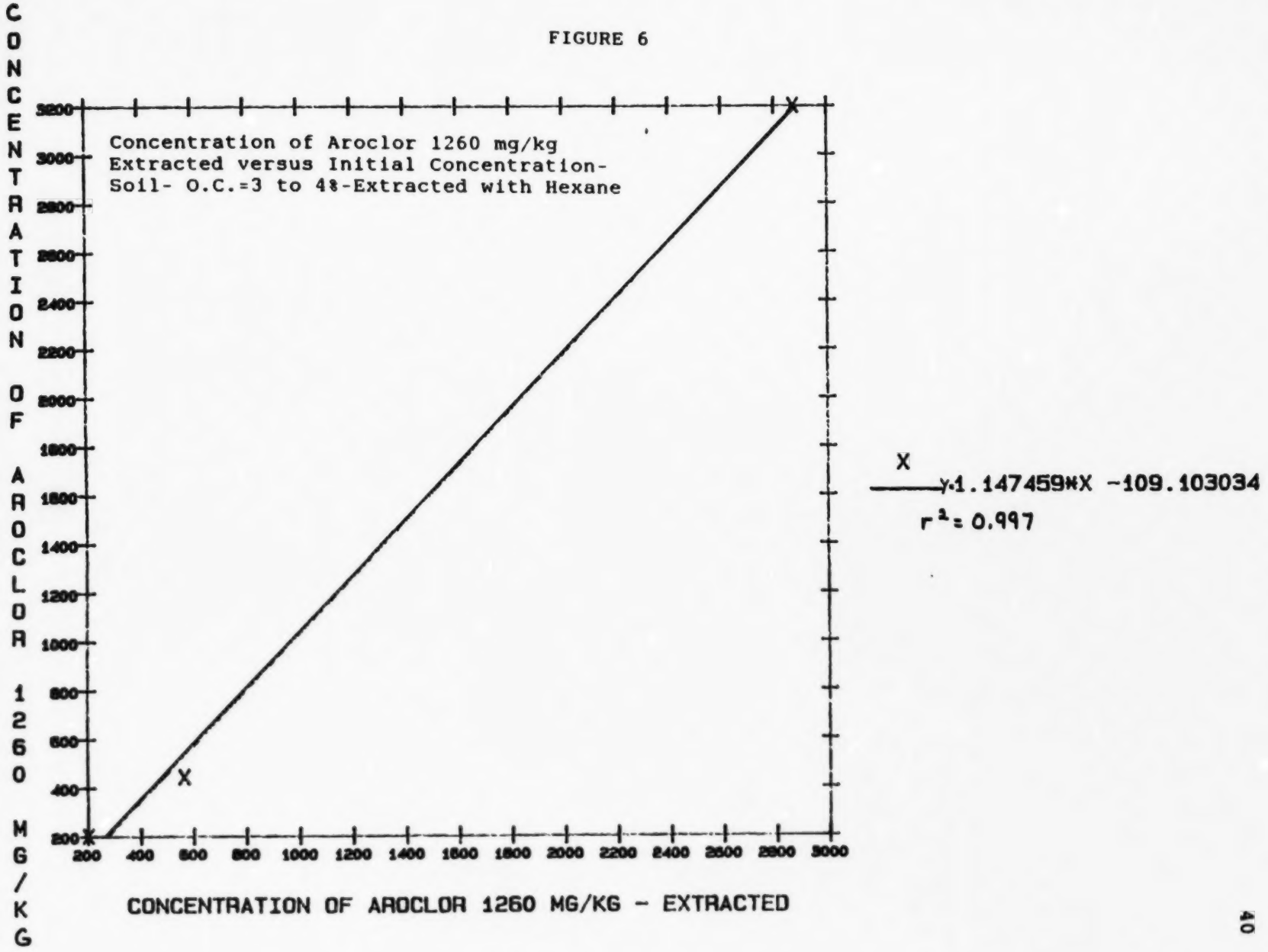
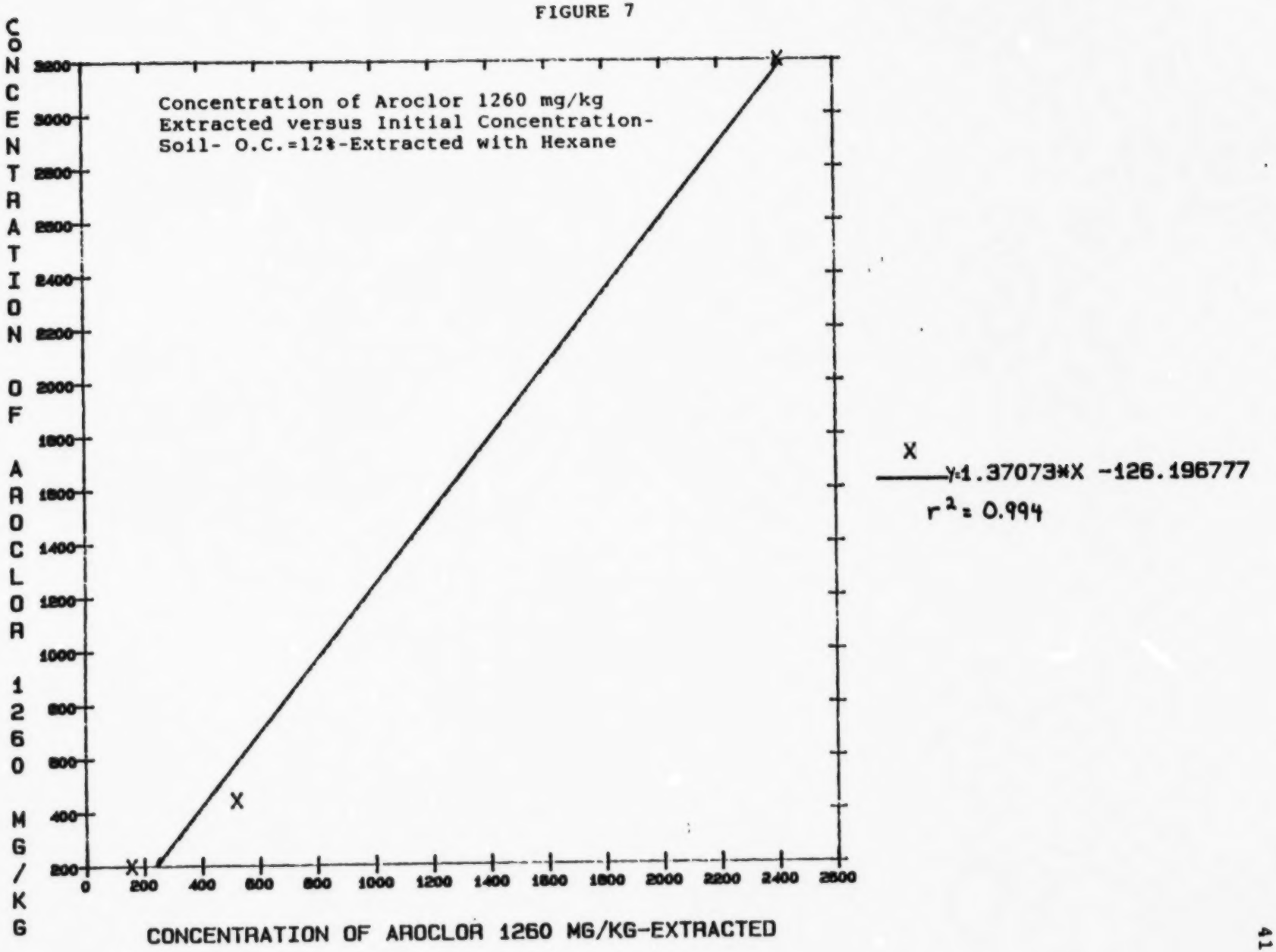

Concentration of Aroclor 1260 mg/kg
Extracted versus Initial Concentration-
Soil- O.C.=3 to 4%-Extracted with Hexane
CONCENTRATION OF AROCLOR 1260 MG/KG
CONCENTRATION OF AROCLOR 1260 MG/KG - EXTRACTED
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
X
Y=1.147459*X -109.103034
r²= 0.997

FIGURE 7



X

$y = 1.37073 * X - 126.196777$

$r^2 = 0.994$

Pentane is more volatile than hexane, and therefore the rate of concentration is increased making the overall procedure faster. PCBs as Aroclor 1260 were detected in soils in a range from 35 ppm to 3200 ppm.

The effects of total organic carbon (TOC) content on PCB extracted with hexane or pentane from the soil were investigated. These results are presented in Figures 2-7. PCBs retended on soils are directly related to TOC contents. These results are consistent with Griffin and Chian (1980), Faraquahar and Sykes (1978), Tucker et al.(1975) and others.

Thus, when taking soils it is important to assess whether the soil is either a sandy soil or a clay soil or a soil high in humic/fulvic acids. If the soil is low in organic carbon one can assume that all or nearly all of the PCBs will be extracted. If the TOC is high, approximately 20% of PCBs may remain on the soil. These numbers should be taken into consideration when determining the concentration of PCBs in soils.

There are several different methods which can be used to correct for the percentage of organic carbon in soils. These are

METHOD 1. Apply the linear regression equations of the actual concentration of Aroclor 1260 versus the concentration of Aroclor 1260 extracted from samples of soils with different amounts of organic carbon:

With soils of organic carbon fraction 0.5%, extracted with hexane

$Y = 1.091 * X + 52.85$

X=Concentration of Aroclor 1260 extracted mg/kg

Y=Actual Concentration of Aroclor 1260 mg/kg

-extracted with pentane

$Y = 1.109 * X - 22.82$

With soils of organic carbon fraction 3-4%, -extracted with hexane

$Y = 1.147 * X - 109.10$

-extracted with pentane

$Y = 1.21 * X - 30.07$

With soils of organic carbon fraction 12-14%, -extracted with hexane

$$Y = 1.371 * X - 126.20$$

-extracted with pentane

$$Y = 1.22 * X + 6.89$$

Results using these modification factors are given in Tables 10 and 11 (Method 1). Applying this modification factor is complex. One must know the linear regression equation and the amount of organic carbon, as well as the solvent used for extraction.

METHOD 2. Apply the linear regression equations which do not separate the soils into different groups, containing different amounts of organic carbon

for those samples extracted with hexane

$$Y = 1.16 * X - 28.43$$

for those samples extracted with pentane

$$Y = 1.17 * X - 13.39$$

Results using these equations are given in Tables 10 and 11 (Method 2). Applying this modification factor is less complex than the previously mentioned one. One needs to know only the linear regression equation for the solvent used for extraction and this difference can probably be averaged, eliminating the requirement to know the solvent used.

METHOD 3. Apply correction factors for soils with different amount of organic carbon

for soils with 0.5% organic carbon

extracted with hexane

Intial Concentration of Aroclor 1260 = Measured Concentration of Aroclor 1260 / 0.91

For Soils with x% organic carbon	Extracted with	Correction Factor
0.5	hexane	0.91
0.5	pentane	1.01
3-4	hexane	1.06
3-4	pentane	0.95
12-14	hexane	0.89
12-14	pentane	0.84

Results are given in Tables 10 and 11 (Method 3).

All of the methods which are mentioned above have correlation coefficients greater than or equal to 0.98 for the linear regression equations of "modified" concentration as determined by chloride determination versus the initial concentrations as determined by ECD. As all the methods appear to be equal in "goodness-of-fit", the best method to choose is the simplest one.

The third method is the simplest method. With this method, one can assume that all or nearly all of the PCBs will be extracted with pesticide grade hexane, if the soil is low in organic carbon. If the soil is high in organic carbon, one can assume that approximately 15% may remain in the soil.

4. Spiking a blank (uncontaminated soil from the same area as the contaminated sample) with a known amount of PCBs. It should be allowed to stand for several hours. The percentage of unextractable PCBs should then be determined and the final concentrations of the test samples should be modified.

How time influenced the results from these methods was not considered. This variable remained constant during this study.

RECOMMENDATIONS

The percentage of PCBs which may be irreversible bonded to organic carbon in the soil should be determined using one of the two following methods.

A. A blank (uncontaminated soil from the same area as the contaminated sample) should be spiked with a known amount of PCBs. It should be allowed to stand for several hours. The percentage of unextractable PCBs should be determined and the final concentrations of the test samples should be adjusted.

B. The type of soil one is dealing with (e.g. soils high or low in organic carbon) should be determined. The amount of sand present in the soil should give an indication of the amount of organic carbon. A high amount of sand indicates a low fraction of organic carbon. A low amount of sand indicates high fraction of organic carbon.

If the soil is low in organic carbon , one can assume that all or nearly all of the PCBs are extracted. No correction factor should be applied to determine the concentration of PCBs in soils.

If the soil is high in organic carbon, one can assume that 15% remains in the soil following extraction. A correction factor should be applied to determine the concentration of PCBs in soils.

Corrected Concentration of Aroclor=Measured Concentration /0.85

CLEANUP

SELECTION OF CLEANUP TECHNIQUES

Cleanup techniques of various transformer oil and PCB-type fluids were investigated by Sonchik et al. (1984). Of these methods, sulfuric acid cleanup was found to be the most effective. This method has also been used by Anhoff and Josefsson (1975), Bellar and Litchenberg (1981) and numerous others. This method was selected for the person-portable analytical system.

EVALUATION/MODIFICATION OF CLEANUP TECHNIQUES

The concentrations of two samples of a PCB transformer oil containing Aroclor 1260 were determined with two different methods of determination. Cleanup techniques were performed on one set of samples and no cleanup techniques were applied to the other.

The cleanup technique consisted of the oil sample being shaken with 5 mL of concentrated sulphuric acid. The phases were allowed to separate and the top layer was removed for PCB analysis. The technique used is described in further detail by Bellar and Litchenberg (1981). The PCBs were determined with a wet test determination which will be described in the proceeding section. Results and experimental conditions for chloride determination are listed in Table 12.

TABLE 12

SULFURIC ACID CLEANUP OF PCB CONTAMINATED TRANSFORMER OILS

Sample No.	With Cleanup Concentration of Aroclor 1260 (ug/mL) Wet Test Det.	With Cleanup Concentration of Aroclor 1260 (ug/mL) GC/ECD	No Cleanup Concentration of Aroclor 1260 (ug/mL) Wet Test Det.
26	83	83	80 n=7

These results indicate that the sulfuric acid cleanup of PCB contaminated transformer oils can be omitted with only a small loss of PCB detection. Omitting it will reduce the number of steps in the experiment and also reduce the hazard to the cleanup crew.

RECOMMENDATIONS

No sulfuric acid cleanup technique should be included.

DETERMINATION

SELECTION OF PCB DETERMINATION TECHNIQUES

The procedure developed by the General Electric Company and the Dexsil Corporation and utilized in the Clor-N-Oil PCB screening kit was selected for evaluation. The Clor-N-Oil kit is based on the quantitative conversion of the chlorine atoms attached to the biphenyl to chloride ions which are in turn extracted into an aqueous solution and measured colorimetrically. Sodium naphthalide in Bis(2-methoxy ethyl) ether is the reagent used to break the carbon-chlorine bonds. The amount of sodium naphthalide reagent plays a key role in determining the success of the chemical dechlorination of PCBs (U.S. Patent #4,284,516,1981). Japanese researchers Oku et al. (1982) have dechlorinated high concentrations of PCBs in tetrahydrofuran. 1.1 to 1.3 moles of sodium naphthalide per mole of chlorine (as Cl) was needed to remove all the organic chlorine. Other researchers have demonstrated that a much higher 100:1 reagent to chlorine mole ratio is necessary to effectively remove PCBs from contaminated oil (U.S. Patents #4,284,516,1981;U.S. Patent #4, 326, 090).

EVALUATION/MODIFICATION OF PCB DETERMINATION TECHNIQUES

Experimental Procedures for Evaluation

The following section details the experimental procedure which was used for the measurement of PCBs in oil. Sections on the required apparatus, glassware, solvents and reagents, packaging requirements and preparation of chemicals are included.

GLASSWARE AND APPARATUS

Separatory Funnel	125 mL
Disposable Pipets	1,5,10 mL
Graduated Cylinder	50 mL
Microburette	1 to 10 mL
pH meter and electrode	
Beakers	10,100 mL
Glass Syringes (luer lock)	10 or 20 mL
Disposable Cellulose Filter Disks, Luer Lock	0.5 um
Glass Funnel, Short Stem	
Filter Paper	
Disposable Latex Gloves	
Portable Cook-It Stove (Hach Kit)	
Magnetic Stirrer-Portable	
Balance	

GLASSWARE CLEANING

As this method was ultimately based on the detection of the chloride anion, it was imperative that all glassware be thoroughly cleaned prior to use. The recommended procedure was to wash all glassware in a detergent solution, followed by rinsings with tap water, then distilled or deionized water and finally with pesticide grade acetone and hexane, or pentane. Glassware was then air dried prior to oven heating.

SOLVENTS AND REAGENTS

The following is a list of solvents and reagents which were required for use. All solvents were pesticide grade and the distilled or deionized water had a conductivity of less than 5 uS/cm.

Acetone
Pentane
Distilled or Deionized Water
Bis (2-methoxy ethyl) ether
Sodium Phosphate
Sodium Metal Dispersion, 10-50 um
Nitric Acid
Mercuric Nitrate

Xylene Cyanol FF
s-diphenylcarbazone
Sodium Chloride
Naphthalene

PACKAGING REQUIREMENTS

1. Bis (2-methoxy ethyl) ether/Naphthalene complex:

This solution was stored in glass and checked frequently for peroxide content. Peroxide test strips were suitable for this purpose. High peroxide content can result in an explosion.

2. Mercuric Nitrate Titrant :

This solution was stored in amber glass.

3. Sodium Metal Dispersion:

Special attention was placed on the handling and dispersing of the sodium dispersion as sodium reacts violently to moisture. This reagent was stored in a plastic container void of air. This container was externally jacketed by an adsorbent.

4. Xylene Cyanol FF/S-diphenylcarbazone indicator:

This alcoholic solution was stored in amber glass.

PREPARATION OF CHEMICAL SOLUTIONS

All of these chemical solutions were prepared in advance.

Mercuric Nitrate Solutions

Various concentrations of mercuric nitrate (approximately 0.0744 M, 0.00744 M and 0.000744 M) were prepared with mercuric nitrate hydrate and water. One concentration could have been used for the various range of concentrations of PCBs which were encountered, preferably 0.0744 M.

Indicator

250 mg of S-diphenylcarbazone and 30 mg of xylene cyanol FF were dissolved in 100 mL of anhydrous alcohol.

Naphthalene/Bis (2-Methoxy Ethyl) Ether

33 grams of naphthalene were dissolved in 100 mL of ether.

Aqueous Buffer

0.18 M NaH_2PO_4 in 0.3 M HNO_3 were prepared by dissolving 24.8 grams of sodium phosphate in 1000 mL of deionized water containing 19

mL of concentrated nitric acid.

1000 mg/L Chloride

2.5 grams of NaCl were oven dried, and then cooled in a dessicator. A solution of 1.6485 grams of NaCl and water was made to 1 litre volumetrically. This solution served as the primary standard for the standardization of the mercuric nitrate solutions.

Standardization of mercuric nitrate solutions was accomplished by titrating 25 mL aliquots of 50, 100 and 1000 mg/L standard chloride solutions. The 1000 mg/L chloride solution was diluted 1:20 anmd 1:10 to obtain the desired concentrations.

PROCEDURES

PCB CONTAMINATED OILS

1. A 10.0 mL aliquot of PCB contaminated oil was pipetted into a 125 mL separatory funnel. A 10.0 mL aliquot of the same oil but diluted 100X with pesticide grade solvent was also pipetted into a 125 mL separatory funnel.

2. A aliquot of 1000 uL of the naphthalene/ether solution was added to the separatory funnels. The separatory funnels were stoppered and the contents were shakened.

3. A aliquot of 1000 uL of sodium metal dispersion to the separatory funnels was added. The separatory funnels were stoppered and the contents were shaken . Any gases that were formed by inverting the separatory funnels were released. The stopcocks were opened. Shaking was continous until all gas formation ceased.

4. With the stopcocks closed, the reaction was allowed to proceed for 5 minutes.

5. A 20.0 mL aliquot of aqueous buffer (0.18M NaH_2PO_4 in 0.3 M HNO_3) was pipeted into the 125 mL separatory funnels.

6. The separatory funnels were stoppered and the contents were shaken . Any gases that were formed by inverting the separatory funnel were released. The stopcocks were opened. Shaking was continuous until all gas formation ceased.

7. The two phases were allowed to separate.

8. The stopcocks were opened and the bottom layers, which were aqueous inorganic phases, were slowly drained into 100 mL beakers.

9. 20 mL of deionized water was added to the 100 mL beakers containing the extracts.

10. Magnetic stirring bars were added and the beakers were placed on magnetic stirring plates.

11. With a calibrated pH electrode, the contents of the 100 mL beakers were adjusted to a pH of 2.5 using HNO_3 (solution diluted 100X) or NH_4OH (solution diluted 100X).

12. The electrode was removed and 1.0 mL of s-diphenylcarbazone/xylene cyanol FF indicator was added. The solutions were blue.

13. The contents of the 100 mL beakers were titrated from a blue to purple endpoint using mercuric nitrate as the titrant.

14. The volumes of titrant used were recorded and one proceeded with the following calculations.

CALCULATIONS

Since the overall reaction for the determination of the chloride ion was

$$Hg + 2\ Cl \rightleftharpoons HgCl_2$$

the number of moles required of Hg was equal to twice the number of moles of Cl .

$$1\ Hg = 2\ Cl$$

An example is included.

EXAMPLE : The concentration of Aroclor 1260 in an oil sample, which had previously been analyzed by gas chromatography and found to contain as its only chlorinated compounds, Aroclor 1260, was determined. 10 ml of this oil was taken and analyzed. The Molarity of the $Hg(NO_3)_2$ solution was 0.0744 mol. The volume of the titrant required to reach an endpoint was 1.73×10^{-3} Litre . The blank was composed of the same materials without the chlorinated compounds. Amount of chlorides in the blank was zero. 18 mL of the 20 mL of buffer solution were titrated.

STEP 1
The number of moles of chloride involved in the reaction was determined.

$$\text{moles of } Hg(NO_3)_2 = \text{Molarity of } Hg(NO_3)_2 \text{ (mol)} \times \text{Volume of Titrant Required to Reach an Endpoint (Litres)}$$

Example: Molarity of $Hg(NO_3)_2$ = 0.0744 mol

Volume of the Titrant Required to Reach Endpoint
= 1.73×10^{-3} Litres

Therefore moles of $Hg(NO_3)_2$ = $0.0744 \times 1.73 \times 10^{-3}$

Step 2

This was converted to an equivalent amount of chloride (Cl^-)
moles of $Hg(NO_3)_2$ X 2 X Molecular Weight of Chlorine (g/mol)
(from Step 1)
= g

Example: Moles of $Hg(NO_3)_2$ determined from Step 1 = 1.289×10^{-4}
Molecular Weight of Chlorine (g/mL) = 35.45

Equivalent Amount of Chlorine = $1.289 \times 10^{-4} \times 2 \times 35.45$

= 9.14×10^{-3} g

STEP 3

This was adjusted for amount of PCB mixture, based on percentage of chlorinated compounds in mixture.

Example: For Aroclor 1260

if 60% was accounted for by 9.14×10^{-3} g
then 100% was equal to 15.22 mg

STEP 4

This was adjusted for amount of PCB, if only part of the aliquot was titrated, or if a dilution was done.

Example: 18 mL of the buffer solution was titrated. This accounted for 90% ,which was equal to 15.22 mg. Therefore 100% was equal to 16.91 mg.

STEP 5

Final sample concentration was determined.

Example: 16.91 mg from a 10 mL Oil Sample
1691 mg in a 1000 mL Oil Sample

STEP 6

This was adjusted for amount present in the blank by subtracting this amount from the sample.

Example: In this case the blank was 0.
No change in concentration.
The final concentration of Aroclor 1260 was 1691 mg/L in this sample of transformer oil.

PROCEDURES

PCB CONTAMINATED SOILS

1. 10 grams of homogeneously mixed, sieved soil samples were weighed and placed in a 125 mL Erlynmeyer flask.

2. 25 mL of pesticide-grade pentane was added to the flasks. The contents were swirled.

3. The contents of the flasks were filtered with Whatman #42 paper filters into 150 mL beakers.

4. Steps 2 and 3 were repeated until a total volume of 100 mL of solvent was used.

5. The solvent mixtures were concentrated to 10 mL using low heat from a portable hot plate or on the small Cook-It stove from the Hach Kit. If less than 10 mL, it was topped up with pesticide grade solvent.

6. The solvent mixtures were transferred to separatory flasks.

7. The same procedure was continued as for the transformer oils with the following exceptions.

8. The concentration of blanks using uncontaminated soils from the same areas as the contaminated sample, was determined.

9. The percentage of PCBs which was irreversibly bonded to organic carbon in the soil was determined. The type of soil one was dealing with (e.g. low or high in organic carbon) was determined. If the soil was low in organic carbon one could assume that all or nearly all of the PCBs were extracted. If the soil was high in organic carbon, approximately 15% was assumed to remain in the soil.

10. Calculations were the same as for oils with the following modifications.

Step 5 Final sample concentrations were determined for
mg/10 g of soil instead of mg/10 mL of oil
mg/kg of soil instead of mg/L of oil

Step 7 Final Concentration of PCBs (mg/kg) = Extracted Concentration of PCBs (mg/kg) / 0.85

Results are listed in Tables 10 and 11.

The first modification to the Clor-N-Oil test was to increase the amounts of metallic sodium and naphthalene in ether in the preparation of the sodium naphthalide reagent and thus increase the amount of sodium naphthalide reagent from that found in the Clor-N-Oil kit. The second modification to the Clor-N-Oil reagent was accomplished by changing the naphthalene to sodium mole ratio from 2:1 to 1:2 thus increasing the amount of free sodium metal. The presence of free sodium metal in the sodium naphthalene formation is known to improve the dechlorination process (U.S. Patent #4, 326, 090,1982).

After the cleavage of the chlorine from the biphenyl the extraction procedures involved the transfer of ionic chloride to an aqueous solution. This was accomplished by adding a known amount of an acidic sodium phosphate buffer to the dechlorinated PCB transformer oil sample. The addition of the acidic buffer effectively quenched the reaction through the destruction of unreacted sodium metal. The oil and aqueous phases were allowed to separate and the bottom layer (aqueous) was removed and analysed for chloride content.

These modifications of the Clor-N-Oil sodium naphthalide reagent proved to be very effective in that a greater reagent to chlorine mole ratio was created, and ultimately a greater range of detection was provided. By modifying the sodium naphthalide reagent, PCBs were effectively dechlorinated in a range of concentrations from 16 to 35,000 ppm, as shown in Table 9,10,11 and 13.

Through the determination of chloride ions the analyst can calculate the amount of PCBs present in a contaminated substance, based on the weight % of chlorine in various Aroclors. The Clor-N-Oil PCB screening kit utilizes the mercuric nitrate method of chloride detection. In this study, modification to the Clor-N-Oil system included changing the indicator used, and titrating chloride to an endpoint with mercuric nitrate.

The indicating compound, s-diphenylcarbazone, was modified slightly by adding xylene cyanol FF to it and titrating the chloride solution from a blue to a purple endpoint. This was done because it was viewed by the analyst that it would make the colour change at the endpoint more distinct. S-diphenylcarbazone alone would make the colour change at the endpoint go from colourless to blue and would be at a pH of 3.1.

The other modification involved titrating chloride to an endpoint with mercuric nitrate. The Clor-N-Oil systems, 0-50 ppm and 0-500 ppm use a fixed amount of mercuric nitrate for PCB determinations and PCB concentrations are determined to be less than or greater than 50/500 ppm, based on the colour formed.By titrating chloride to an endpoint with mercuric nitrate, greater accuracy is provided, and specific PCB concentrations can be generated. Figures 8 to 10 are graphs of the concentration of Aroclor 1260 versus the titrant volume of 0.0744 M of mercuric nitrate at different volumes of oil aliquots (e.g. 1 and 10 mL). They are linear over a wide range of concentrations.

This method determines the chlorine/chloride content present. If separation from other chlorinated compounds (e.g. trichlorobenzenes) is not part of the procedure, as was done in

this case, then these methods will lead to errors in the determination of PCB content as compared to the GC/ECD determination and the chloride determination. In addition, differences in the average chlorine content for the various Aroclor mixtures further introduces inherent errors because of average molecular weights even when correction for or elimination of the trichlorobenzene interferences are made. This fact must be taken into consideration when trying to assign a concentration to PCB contaminated materials. In this study, testing was only performed on oils containing Aroclor 1260. Lower limits of detections will suffer when analysing for less chlorinated Aroclors such as 1254 and 1242.

As the acquisition of pure Aroclor standards was impossible due to cost and availability PCB contaminated transformer oils were substituted for use. Many electrical insulating medias contain trichlorobenzenes. These chlorinated aromatics undergo carbon-chlorine bond cleavage when subjected to organo-metallic compounds such as sodium naphthalide.

In this study it appears that the lower concentrations of PCBs as determined by chloride determination are closer in value to the GC/ECD determinations than are the higher concentrations. At high concentrations there may be a certain amount of quenching. It is therefore suggested that dilutions of 100X with pesticide-grade solvents, should be undertaken at the same time as the undiluted samples are tested. The concentration determined by means of the dilution may be a closer approximation to the actual concentration.

Table 14 is a comparison of the concentrations of PCBs contaminated oils by various methods. If one assumes that the most accurate method of detection is by GC/ECD, then the method that most closely falls in line with these readings is the method described in this report. This is especially true for high concentrations.

RECOMMENDATIONS

The experimental procedure as described in the preceeding section should be used to determine the concentration of PCBs in a person portable analytical test kit.

TABLE 13

PCB DETERMINATION OF PCB CONTAMINATED TRANSFORMER OILS FOR LOWER LIMITS OF DETECTION

Sample No.	Concentration of Aroclor 1260 determined by Chloride Determination	Concentration of Aroclor 1260 determined by GC/ECD
56	17	18
57	18	20
58	21	23
62	17	16
64	21	16
65	22	19

FIGURE 8

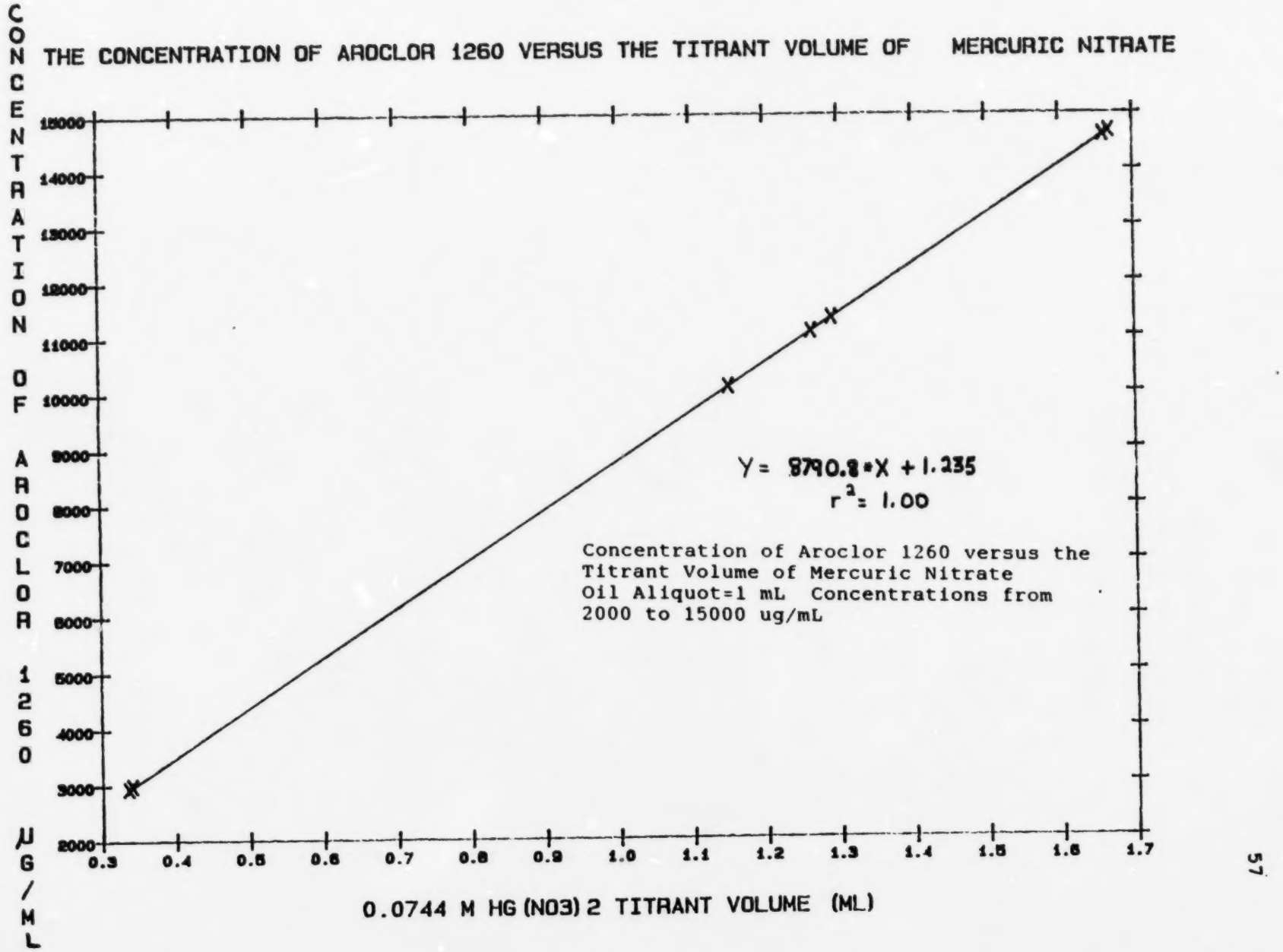

THE CONCENTRATION OF AROCLOR 1260 VERSUS THE TITRANT VOLUME OF MERCURIC NITRATE
CONCENTRATION OF AROCLOR 1260 UG/ML
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
Y= 8790.8*X + 1.235
r2= 1.00
Concentration of Aroclor 1260 versus the Titrant Volume of Mercuric Nitrate Oil Aliquot=1 mL Concentrations from 2000 to 15000 ug/mL
0.0744 M HG(NO3)2 TITRANT VOLUME (ML)

FIGURE 9

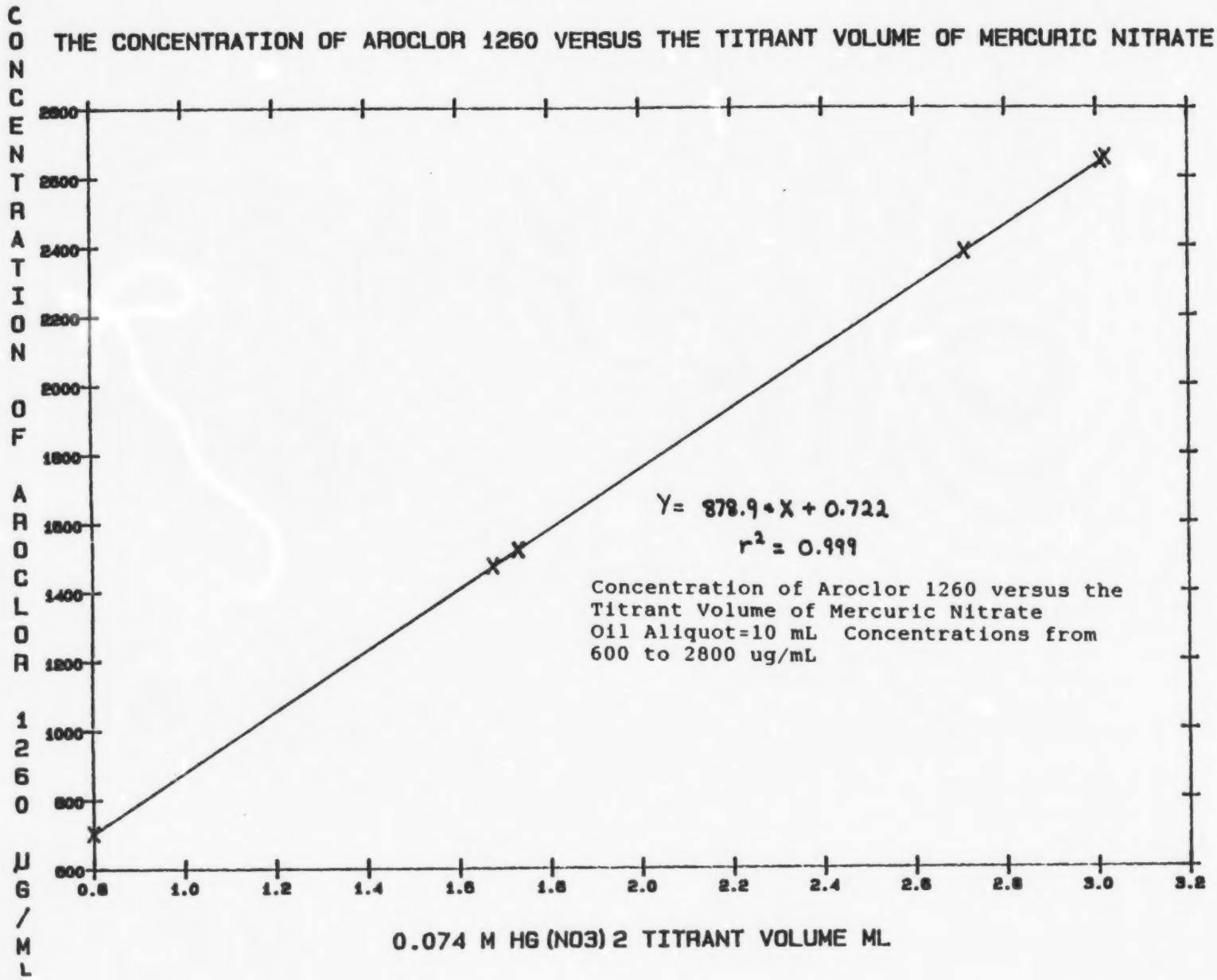

THE CONCENTRATION OF AROCLOR 1260 VERSUS THE TITRANT VOLUME OF MERCURIC NITRATE
CONCENTRATION OF AROCLOR 1260 UG/ML
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
Y= 878.9*X + 0.722
r² = 0.999
Concentration of Aroclor 1260 versus the Titrant Volume of Mercuric Nitrate
Oil Aliquot=10 mL Concentrations from 600 to 2800 ug/mL
0.074 M HG(NO3)2 TITRANT VOLUME ML

FIGURE 10

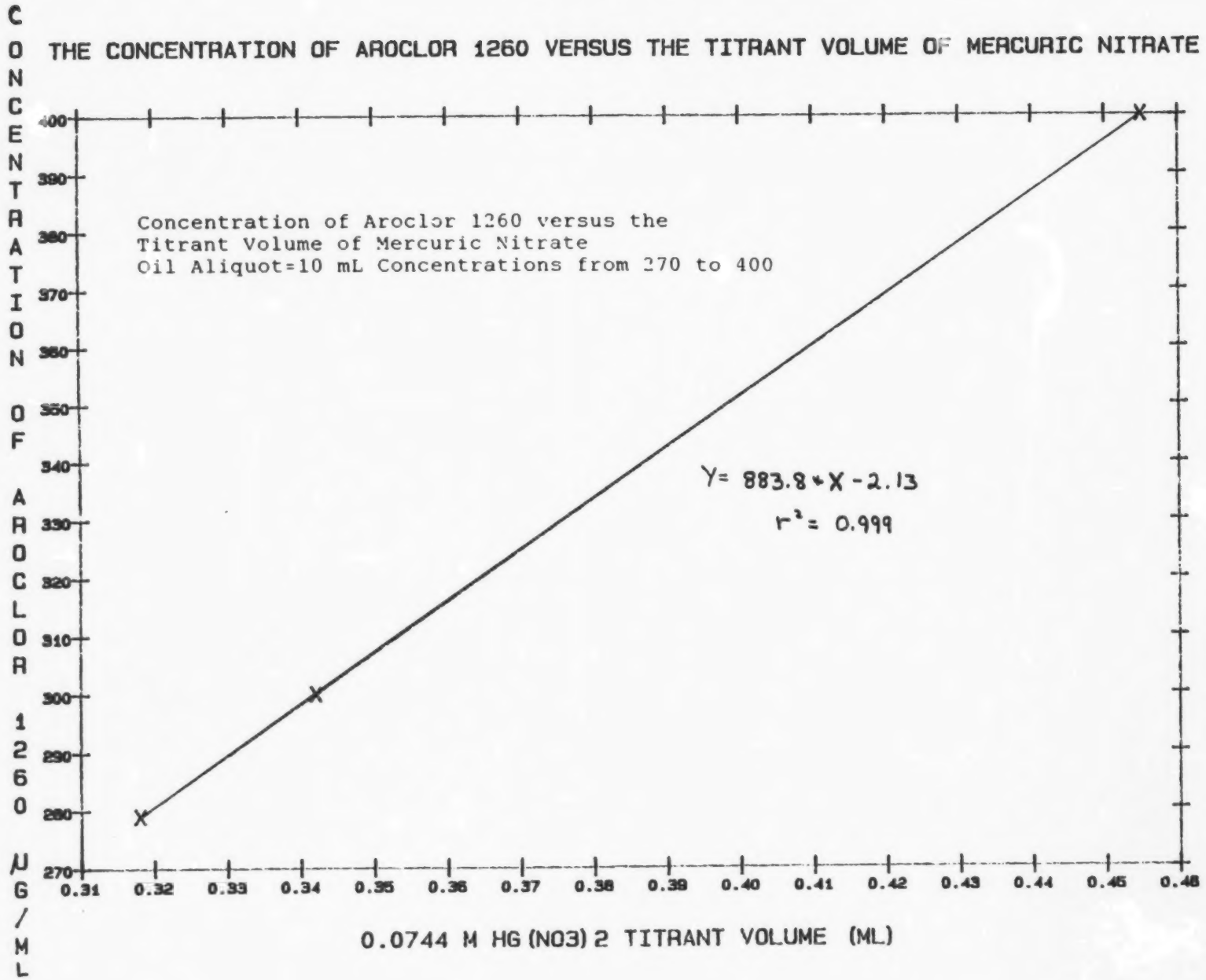

THE CONCENTRATION OF AROCLOR 1260 VERSUS THE TITRANT VOLUME OF MERCURIC NITRATE
Concentration of Aroclor 1260 versus the
Titrant Volume of Mercuric Nitrate
Oil Aliquot=10 mL Concentrations from 270 to 400
Y= 883.8*X -2.13
r² = 0.999
CONCENTRATION OF AROCLOR 1260 UG/ML
INITIAL
400
390
380
370
360
350
340
330
320
310
300
290
280
270
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
0.39
0.40
0.41
0.42
0.43
0.44
0.45
0.46
0.0744 M HG(NO3)2 TITRANT VOLUME (ML)

TABLE 14

COMPARISON OF CONCENTRATIONS OF PCB CONTAMINATED OILS BY VARIOUS METHODS

Sample No.	Centec	Kwik-Skrene	Clor-N-Oil	GC/ECD	This Study
12	102	>35	>50	151	300
26	40	>35		83	115 88
39	151	>35		134	172 220
40	163	>35	>50	126	180
54	27	>35		16	
56	18	>35		18	17
57	20	>35		20	18
58	23	>35		23	21
62	16	>35		16	17
64	16	>35		16	21
65	19	>35		19	22
72	25	>35		59	
78	14	>35			
83	22	>35			
84	1046	>35	>50	4445	2992 2945 7030
85	1046	>35		20088	10110 11340 12500 15220 15210 16900 14750 27900 30000 40000
86	1046	>35		35599	14660 11095

14600
23830
26550
26450
19280
49300

SUMMARY

RECOMMENDED PERSON PORTABLE ANALYTICAL SYSTEM

COLLECTION

Solid sampling

When soil, sand or sediment samples are to be taken, a surface scrape sample of approximately 1 cm should be collected with a trowel or similar implement, preferably stainless steel. The sample should be scraped directly into a precleaned glass bottle and weighed. If it is free flowing, the sample should be thoroughly homogenized by shaking. If not, the sample should be mixed to create a representative sub-sample. For samples, such as sod, core samples not more than 5 cm deep should be taken using a soil coring device. Before collection of verification samples, the equipment should be used to generate a field blank.

Water Sampling

Surface Sampling

If PCBs dissolved in a hydrocarbon oil are spilled, they will most likely be dispersed on the surface. Therefore, a surface water collection technique must be used. Surface water samples should be collected by grab techniques. When appropriate, the precleaned glass sample bottle may be dipped directly into the body of water at the designated sample collection point. A sample is collected from the water surface by gently lowering a precleaned sample bottle horizontally into the water until water begins to run into it. The bottle is then slowly turned upright keeping the lip just under the surface so that the entire sample is collected from the surface.

Subsurface Sampling

If the PCBs are in an Askarel or other heavier-than-water matrix, the PCBs will sink. In these cases water near the bottom should be collected. To collect subsurface water, the bottle should be lowered to the specified depth with the cap on. The cap is then removed, the bottle allowed to fill, and the bottle brought to the surface.

Other Sampling Approaches

When the above approaches are not feasible, other dippers, tubes, siphons, pumps, etc., may be used to transfer the water to sample bottle. The sampling system should be of stainless steel, Teflon, or other inert, impervious and noncontaminated material. Before collection of samples, this equipment must be used to generate a field blank.

Surface Sampling

Wipe Sampling

Smooth and impervious surfaces should be sampled by first applying an appropriate solvent (e.g. hexane) to a piece of 11 cm filter paper (e.g. Whatman 40 ashless, Whatman "50" smear tabs, or equivalent) or gauze pad. This moistened filter paper or gauze pad is held with a pair of stainless steel forceps and used to thoroughly swab a 100 cm area as measured by a sampling template. Before collection of verification samples, the selected filter paper or gauze pad and solvent should be used to generate a field blank.

Sampling Porous Surfaces

Wipe sampling is inappropriate for surfaces which are porous and would absorb PCBs. These include wood and asphalt. Where possible, a discrete object (e.g., a paving brick) may be removed. Otherwise, chisels, drills, saws, etc., may be used to remove a sufficient sample for analysis. Samples less than 1 cm deep on the surface most likely to be contaminated with PCBs should be collected.

Vegetation Sampling

The sample design or visual inspection may indicate that samples of vegetation (such as leaves, bushes and flowers) are required. In this case, samples may be taken with pruning shears,a saw or other suitable tool and placed in a precleaned glass bottle.

STORAGE

None required.

WARNING!

THIS ANALYTICAL METHOD IS NON-SPECIFIC IN REGARDS TO IDENTIFYING AROCLOR TYPES. OTHER CHLORINATED AROMATICS, SUCH AS TRICHLOROBENZENES, ALSO REACT AND INCREASE THE FINAL PCB CONCENTRATION.

DETERMINATION

GLASSWARE AND APPARATUS

Separatory Funnel	125 mL
Disposable Pipets	1,5,10 mL
Graduated Cylinder	50 mL
Microburette	1 to 10 mL
pH meter and electrode	
Beakers	10,100 mL
Glass Syringes (luer lock)	10 or 20 mL
Disposable Cellulose Filter Disks, Luer Lock	0.5 um
Glass Funnel, Short Stem	
Filter Paper	
Disposable Latex Gloves	
Portable Cook-It Stove (Hach Kit)	
Magnetic Stirrer-Portable	
Balance	

GLASSWARE CLEANING

As this method is ultimately based on the detection of the chloride anion, it is imperative that all glassware be thoroughly cleaned prior to use. The recommended procedure is to wash all glassware in a detergent solution, followed by rinsings with tap water, then distilled or deionized water and finally with pesticide grade acetone and hexane, or pentane. Glassware is then air dried prior to oven heating.

SOLVENTS AND REAGENTS

The following is a list of solvents and reagents which are required for use. All solvents are pesticide grade and the distilled or deionized water has a conductivity of less than 5 uS/cm.

Acetone
Pentane
Distilled or Deionized Water
Bis (2-methoxy ethyl) ether
Sodium Phosphate
Sodium Metal Dispersion, 10-50 um
Nitric Acid
Mercuric Nitrate
Xylene Cyanol FF
s-diphenylcarbazone
Sodium Chloride
Naphthalene

PACKAGING REQUIREMENTS

1. Bis (2-methoxy ethyl) ether/Naphthalene complex:

This solution is stored in glass and checked frequently for peroxide content. Peroxide test strips are suitable for this purpose. High peroxide content can result in an explosion.

2. Mercuric Nitrate Titrant :

This solution is stored in amber glass.

3. Sodium Metal Dispersion:

Special attention is placed on the handling and dispersing of the sodium dispersion as sodium reacts violently to moisture. This reagent is stored in a plastic container void of air. This container is externally jacketed by an adsorbent.

4. Xylene Cyanol FF/s-diphenylcarbazone indicator:

This alcoholic solution is stored in amber glass.

PREPARATION OF CHEMICAL SOLUTIONS

All of these chemical solutions are prepared in advance.

Mercuric Nitrate Solutions

Various concentrations of mercuric nitrate (approximately 0.0744 M, 0.00744 M and 0.000744 M) are prepared with mercuric nitrate hydrate and water. One concentration could be used for the various range of concentrations of PCBs which are encountered, preferably 0.0744 M.

Indicator

250 mg of s-diphenylcarbazone and 30 mg of xylene cyanol FF are dissolved in 100 mL of anhydrous alcohol.

Naphthalene/Bis (2-Methoxy Ethyl) Ether

33 grams of naphthalene are dissolved in 100 mL of ether.

Aqueous Buffer

0.18 M NaH_2PO_4 in 0.3 M HNO_3 are prepared by dissolving 24.8 grams of sodium phosphate in 1000 mL of deionized water containing 19 mL of concentrated nitric acid.

1000 mg/L Chloride

2.5 grams of NaCl are oven dried, and then cooled in a

dessicator. A solution of 1.6485 grams of NaCl and water is made to 1 litre volumetrically. This solution serves as the primary standard for the standardization of the mercuric nitrate solutions.

Standardization of mercuric nitrate solutions are accomplished by titrating 25 mL aliquots of 50, 100 and 1000 mg/L standard chloride solutions. The 1000 mg/L chloride solution are diluted 1:20 and 1:10 to obtain the desired concentrations.

PROCEDURES

PCB CONTAMINATED OILS

1. A 10.0 mL aliquot of PCB contaminated oil is pipetted into a 125 mL separatory funnel. A 10.0 mL aliquot of the same oil but diluted 100X with pesticide grade solvent is also pipetted into a 125 mL separatory funnel.

2. An aliquot of 1000 uL of the naphthalene/ether solution is added to the separatory funnels. The separatory funnels are stoppered and the contents are shaken.

3. To the separatory funnels 1000 uL of sodium metal dispersion is added. The separatory funnels are stoppered and the contents are shaken. Any gases that are formed are released. Shaking is continued until all gas formation ceases.

4. With the stopcocks closed, the reaction is allowed to proceed for 5 minutes.

5. A 20.0 mL aliquot of aqueous buffer (0.18M NaH_2PO_4 in 0.3 M HNO_3) is pipetted into the 125 mL separatory funnels.

6. The separatory funnels are stoppered and the contents are shaken. Any gases that are formed are released. Shaking is continued until all gas formation ceases.

7. The two phases are allowed to separate.

8. The stopcocks are opened and the bottom layers, which are aqueous inorganic phases, are slowly drained into 100 mL beakers.

9. 20 mL of deionized water is added to the 100 mL beakers containing the extracts.

10. Magnetic stirring bars are added and the beakers are placed on magnetic stirring plates.

11. With a calibrated pH electrode, the contents of the 100 mL beakers are adjusted to a pH of 2.5 using HNO_3 (solution diluted 100X) or NH_4OH (solution diluted 100X).

12. The electrode is removed and 1.0 mL of s-

diphenylcarbazone/xylene cyanol FF indicator is added. The solutions are blue.

13. The contents of the 100 mL beakers are titrated from a blue to purple endpoint using mercuric nitrate as the titrant.

14. The volumes of titrant used are recorded and one proceeds with the following calculations.

CALCULATIONS

STEP 1
The number of moles of chloride involved in the reaction is determined.

$$\text{moles of } Hg(NO_3)_2 = \frac{\text{Molarity of } Hg(NO_3)_2}{\text{mol}} \times \text{Volume of Titrant Required to Reach an Endpoint (Litres)}$$

Step 2

This is converted to an equivalent amount of chloride (Cl^-)
moles of $Hg(NO_3)_2$ X 2 X Molecular Weight of Chlorine (g/mol)
(from Step 1)
= g

STEP 3

This is adjusted for amount of PCB mixture, based on percentage of chlorinated compounds in mixture.

STEP 4

This is adjusted for amount of PCB, if only part of the aliquot is titrated, or if a dilution is done.

STEP 5

Final sample concentration is determined.

STEP 6

This is adjusted for amount present in the blank by subtracting this amount from the sample.

An example is given in the previous section.

PCB CONTAMINATED SOILS

1. 10 grams of homogeneously mixed, sieved soil samples are weighed and placed in a 125 mL Erlynmeyer flask.

2. 25 mL of pesticide-grade pentane is added to the flasks. The contents are swirled.

3. The contents of the flasks are filtered with Whatman #42 paper filters into 150 mL beakers.

4. Steps 2 and 3 are repeated until a total volume of 100 mL of solvent is used.

5. The solvent mixtures are concentrated to 10 mL using low heat from a portable hot plate or on the small Cook-It stove from the Hach Kit. If less than 10 mL, it is topped up with pesticide grade solvent.

6. The solvent mixtures are transferred to separatory flasks.

7. The same procedure is continued as for the transformer oils with the following exceptions.

8. The concentration of blanks using uncontaminated soils from the same areas as the contaminated sample, is determined.

9. The percentage of PCBs which is irreversibly bonded to organic carbon in the soil is determined. The type of soil one is dealing with (e.g. low or high in organic carbon) is determined. If the soil is low in organic carbon one could assume that all or nearly all of the PCBs are extracted. If the soil is high in organic carbon, approximately 15% is assumed to remain in the soil.

10. Calculations are the same as for oils with the following modifications.

Step 5 Final sample concentrations are determined for mg/10 g of soil instead of mg/10 mL of oil
mg/kg of soil instead of mg/L of oil

Step 7 Final Concentration of PCBs (mg/kg) = Extracted Concentration of PCBs (mg/kg) / 0.85

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